DEVELOPMENT, CHARACTERIZATION, AND APPLICATION OF THE DRI MODEL 2015 MULTIWAVELENGTH THERMAL-OPTICAL CARBON ANALYZER

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Atmospheric Sciences

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August, 2015
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DESIGN, DEVELOPMENT, CHARACTERIZATION, AND APPLICATION OF THE
DRI MODEL 2015 MULTIWAVELENGTH CARBON ANALYZER

be accepted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

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ABSTRACT
A multiwavelength thermal/optical carbon analyzer (DRI Model 2015) equipped with a novel seven-wavelength light source (405, 445, 532, 635, 780, 808, and 980 nm) was developed to analyze chemical and optical properties of carbonaceous particles collected on quartz-fiber filters. Built upon the DRI Model 2001 carbon analyzer at 633 nm, major modifications were made to mechanical and electrical components, flow control, and the carbon detector to adopt modern technologies, increase instrument reliability, and reduce costs and maintenance. This instrument quantifies organic and elemental carbon (OC and EC, respectively) and their thermal fractions. It also allows estimation of the amount of brown and black carbon (BrC and BC, respectively) on filters. Continuous monitoring of the light reflected from and transmitted through the filter along with carbon evolved from the filter when heated to different temperatures under either inert or oxidizing gas environments provides insights into the optical properties of the carbon released from the filter; it also allows examination of the charring process as pyrolyzed char has been one of the major uncertainties in quantifying OC and EC. The objectives of this study are: 1) characterize the Model 2015’s performance parameters including detection limits, and optical behavior; 2) establish performance equivalence between the Model 2015 and Model 2001 DRI carbon analyzers when comparing similar laser wavelength to maintain consistency for long-term network sample analysis; and 3) conduct a preliminary analysis of the multiwavelength signal to estimate BrC and BC, and to optimize char correction. A selection of samples, including standard chemicals, as well as rural and urban ambient filter samples were measured by both the Model 2015 and Model 2001 analyzers. The design and construction experience will be discussed, as well as recommended future scientific research and engineering development.
DEDICATION

To my mother, who knew I could do it.
ACKNOWLEDGEMENTS

The development of the Model 2015 was a team effort. Many people contributed countless hours of effort to create this instrument and help with its characterization and application. The author would like to acknowledge:

- **Drs. Judith Chow & John Watson** for their overall vision, guidance, and support
- **Dr. Xiaoliang Wang** for technical management, support, and mentoring
- **Dr. L.-W. Antony Chen** for insightful interpretation of optical data
- **Dr. William P. Arnott** for fundamental guidance
- **Jerome Robles** for laying the groundwork for Model 2015
- **Steve Kohl & Dana Trimble** for laboratory management and support
- **Steven Gronstal & Keith Szelagowski** for software and database development
- **Sierra Mayorga, Matt Thompkins, Joseph Knue, and Rick Purcell** for assembly, calibration, testing, and improvements
- **Patrick Hurbain** for standard preparation and sample analysis
- **All the carbon lab technicians** who kept Model 2015 running all night long
# CONTENTS

1 Introduction .................................................................................................................. 1  
1.1 Background .................................................................................................................. 1  
1.2 Thermal/Optical Analysis .............................................................................................. 4  
1.3 Overview of this Research ........................................................................................... 8  

2 Design of the DRI Model 2015 Multiwavelength Carbon Analyzer ......................... 11  
2.1 Motivation .................................................................................................................... 11  
2.2 Principle of Operation .................................................................................................. 12  
2.3 Instrument Design ....................................................................................................... 19  
2.3.1 Addressing the Design Criteria ............................................................................... 19  
2.3.2 Prototyping with 3D Printers .................................................................................. 26  
2.3.3 Design of the Seven-Wavelength Optical System .................................................. 28  
2.4 Instrument Setup and Calibration ................................................................................. 36  
2.4.1 Optical Power Adjustment and Oven Glow Mitigation .......................................... 36  
2.4.2 Thermal Calibration and Optimization .................................................................... 38  
2.4.3 Mass Flow Calibration .............................................................................................. 39  
2.4.4 Carbon Calibration ................................................................................................... 40  
2.5 Summary ...................................................................................................................... 42  

3 Characterization of the Model 2015 Multiwavelength Carbon Analyzer ................. 43  
3.1 Detection limits .......................................................................................................... 43  
3.1.1 Minimum detection limit ......................................................................................... 43  
3.1.2 Upper detection limit and Linear Range .................................................................. 44  
3.2 Calibration of Reflectance and Transmittance Signals .............................................. 47  
3.3 Equivalence between Model 2015 and Model 2001 ................................................ 55  
3.4 Summary ...................................................................................................................... 67  

4 Application of the DRI Model 2015 Multiwavelength Carbon Analyzer to Ambient Samples ......................................................................................................................... 68  
4.1 Wavelength Dependence and Consistency of the OC/EC Split .................................. 68  
4.2 Absorption Efficiencies and Apportionment of EC and POC in Ambient Samples ........ 72  
4.2.1 Methods .................................................................................................................. 72  
4.2.2 Results and Discussion ............................................................................................ 73
### 4.3 Preliminary Testing with Different Thermal/Optical Protocols

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.1 Description and implementation of different protocols</td>
<td>83</td>
</tr>
<tr>
<td>4.3.2 Results</td>
<td>88</td>
</tr>
</tbody>
</table>

### 4.4 Summary

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
</tr>
</tbody>
</table>

### 5 Conclusions and Future Work

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
</tr>
</tbody>
</table>

### 5.1 Future research questions

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.1 Black carbon aggregates on filter media during thermal evolution</td>
<td>99</td>
</tr>
<tr>
<td>5.1.2 Additional considerations for the multiwavelength light source</td>
<td>99</td>
</tr>
<tr>
<td>5.1.3 Partitioning BC, BrC, and POC</td>
<td>100</td>
</tr>
<tr>
<td>5.1.4 Use of multiwavelength reflectance data</td>
<td>100</td>
</tr>
<tr>
<td>5.1.5 Functionality of the side-arm oxygen injector</td>
<td>100</td>
</tr>
</tbody>
</table>

### 6 References

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
</tr>
</tbody>
</table>

### 7 Appendices

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Appendix I –Electrical Schematic and Layout of the Laser PCB</td>
<td>114</td>
</tr>
<tr>
<td>7.2 Appendix II –Multiwavelength Retrofit for Model 2001 Analyzers</td>
<td>119</td>
</tr>
</tbody>
</table>
Table of Figures

Figure 1-1: Classification of carbonaceous aerosol components based on thermochemical and optical properties as well as molecular structure (Pöschl, 2003). ........................................... 2

Figure 1-2: Example thermogram showing temperature, optical and NDIR responses, and sample oven pressure. ........................................................................................................... 6

Figure 2-1: Schematic diagrams of the upper (a) and lower (b) sections of the Model 2015. ................................................................................................................................. 13

Figure 2-2: Photographs of the instrument. Top: the instrument with cover on. Bottom: analyzer interior showing sample loading hardware, temperature controllers, and sample cooling fan. .................................................................................................................. 14

Figure 2-3: Arrangement of the sample analysis region, showing optical path and oxidation reactor. ....................................................................................................................... 17

Figure 2-4: Optical configurations for: a) Model 2001; and b) Model 2015. Mechanical modulation of the 633 nm helium-neon (He-Ne) laser is replaced by sequential pulse modulation of seven diode lasers. The aerosol deposit faces the incident radiation in both cases. The single optical fiber in the Model 2015 provides more efficient light transmission than the optical fiber bundle in the Model 2001. ........................................... 21

Figure 2-5: Model 2001 quartz cross with a single-bulb oxidation oven shown (shaded region). ................................................................................................................................. 24

Figure 2-6: Model 2015 with quartz cross with a double-bulb oxidation oven (shaded region). The presence of O₂ in both OC and EC analysis stage as well as the larger volume of MnO₂ ensure conversion of carbon to CO₂. Volume shown is the total volume of the catalyst. ................................................................................................................................. 24

Figure 2-7: Plastic parts 3D-printed for the Model 2015 (pictures not to scale): a) Sample oven fan holder; b) CO₂ scrubber holders; c) reflectance photodiode holder; d) bracket for 8-furcated fiber optic cable, and e) laser holder and cover. ....................................... 27

Figure 2-8: Arrangement of light source, detectors, and modulation/extraction algorithm. ................................................................................................................................. 29

Figure 2-9a-g: The laser control board design iterations. ........................................... 35

Figure 2-10: Comparison of NIST and Tempilaq methods from calibration of a Model 2015. ................................................................................................................................. 39

Figure 2-11: Pneumatic diagram of Model 2015 Carbon Analyzer. Numbers on the diagram represent the flow at that point and are in mL/min. The large orange region represents the double-bulb MnO₂ reactor showing He2 or He/O₂ injected into the center. 40

Figure 2-12a: Example carbon calibration with individual standards identified. ....... 41

Figure 3-1: Linearity tests with sucrose standards. Strong correlation with the 1:1 line is observed over several decades, while below the MDL results deviate. R² for the regression is 0.996. Axes are logarithmic, the blue line is the 1:1 line, and the black dotted line is the least-squares regression line. ................................................................. 41

Figure 3-2: Linearity test of the FID with the same standards from the NDIR test. .... 46

Figure 3-3: Thermogram of 10 µl aliquot of 100000ppm solution. The OC3 peak nearly reaches 12000 ppm CO₂, far above the manufacturer's stated 2000 ppm range. ....... 46
Figure 3-4: Optical transfer standard filter samples used in this study. The far left sample is the blank from each batch. .......................... 49
Figure 3-5: Optical calibration of transfer standard samples determined with a calibrated UV/VIS spectrophotometer. Sample loadings increase for higher-numbered samples. Vertical lines designate the seven wavelengths in Model 2015. .......................... 52
Figure 3-6: Reflectance (a and b) and transmittance (c and d) calibration curves derived from LR and LT by Model 2015 (a and c) and Model 2001 (b and d) and FR and FT by Lambda UV/VIS spectrometer. The laser signals are a constant factor of millivolt photodetector outputs normalized to a common scale for all wavelengths. The factors for Model 2015 and Model 2001 are different due to their different optical setup. .......................... 54
Figure 3-7: Trends in annual average organic carbon (OC) and elemental carbon (EC) concentrations at the Shenandoah National Park IMPROVE site. The red line indicates the year (CY 2005) when the Model 2001 thermal/optical carbon analyzer replaced the DRI/OGC carbon analyzers. Data were obtained from CIRA (2014). .......................... 56
Figure 3-8. Replicate analyses of IMPROVE (x-module) samples (N = 17) on Model 2001 (left panels) and Model 2015 (right panels). OC1, OC2, OC3, and OC4 are organic carbon evolved at 140, 280, 480, and 580 °C, respectively, in a 100% He atmosphere. EC1, EC2, and EC3 are elemental carbon evolved at 580, 740, and 840 °C, respectively, in a 98% He / 2% O2 atmosphere. OP is pyrolyzed organic carbon by reflectance (OPR) or transmittance (OPT). OCR = (OC1 + OC2 + OC3 + OC4) + OPR. OCT = (OC1 + OC2 + OC3 + OC4) + OPT. ECR = (EC1 + EC2 + EC3) – OPR. ECRT = (EC1 + EC2 + EC3) – OPT. TC = OC + EC. .......................................................... 58
Figure 3-9: Comparison of Models 2001 and 2015 for Fresno (n = 67), IMPROVE (n = 71), and IMPROVE X modules (n = 73) samples. ........................................ 63
Figure 3-10: Comparison of OC and EC (by reflectance) from IMPROVE samples collected during 2010-2013 and during 2005-2009 analyzed by Models 2001 and 2015. ........................................ 67
Figure 4-1a: Comparison of [carbon] after O2 with the maximum attenuation at 635 nm. The absorption efficiencies of EC and POC are estimated from multiple linear regression. .......................................................... 76
Figure 4-2a: EC/POC partition at 405 nm. Red and black overlays are EC from transmittance and reflectance, respectively. .......................................................... 79
Figure 4-3: Power law regression for determining AAE of EC and POC based on absorption efficiencies (n=139). .......................................................... 83
Figure 4-4: Example thermograms for: a) IMPROVE_A, b) NIOSH, c) STN, and d) EUSAAR_2 thermal/optical protocols on Model 2015 for Fresno sample #FSH00099. .......................................................... 87
Figure 4-5: TC comparison of the protocols. .......................................................... 89
Figure 4-6: Comparison of OCR/ ECR by IMPROVE_A with OCT/ECT by other protocols.......................................................... 92
Figure 4-7: Comparison of TOR by all protocols and wavelengths. .......................................................... 94
Figure 4-8: Comparison of TOT by all protocols and wavelengths. .......................................................... 96
Figure 5-1: Chromatogram with oxygen available through the side-arm. ........................................ 102
Figure 5-2: Chromatogram with side-arm switched off............................................. 103
Figure 7-1a: The hierarchy of the laser PCB................................................................. 114
Figure 7-2: Photograph of the first retrofit unit. This unit was installed at a laboratory in Rostock, Germany ............................................................................................................ 120
Figure 7-3: The drop-in replacement retrofit with VHDCI pass-through from Model 2001 to LabView ................................................................................................................................................... 120
Figure 7-4: The drop-in retrofit installed in Model 2001 with components labeled. ..... 121
List of Tables
Table 2-1: List of key design differences between Models 2001 and 2015. 20
Table 3-1: Models 2015 minimum detection limits for OC, EC, and TC. 43
Table 3-2: Comparison of Fresno, IMPROVE, and IMPROVE X modules samples measured by the Models 2001 and 2015 following the IMPROVE_A protocol (x is Model 2001 and y is Model 2015). 65
Table 4-1: Fresno ambient samples analyzed by Model 2015 for optical pyrolysis. x and y are wavelengths of the seven-wavelength light source; x is 635 nm and y are the new wavelengths available for analysis. This table shows comparisons of new wavelengths to the 635 nm. m and b are Deming regression slope and intercept. n=137. 69
Table 4-2: ECR for source samples. 70
Table 4-3: ECT for source samples. 71
Table 4-4: Absorption efficiencies of EC and POC and their ratios per wavelength for the Fresno samples. 74
Table 4-5: Regression of ECR and ECT vs. partitioned EC at each wavelength. 83
Table 4-6: Comparison of thermal/optical protocols (adapted from Chow et. al., 2001 and 2014). 84
Table 4-7. OC and EC Deming statistics averaged across all seven wavelengths. 92
Table 4-8: Summary of TOR statistics averaged across all wavelengths. 94
Table 4-9: Summary of TOT statistics averaged across all wavelengths. 96
Table 5-1: Summary of NDIR results for the five tests (average ± standard deviation). 102
1 INTRODUCTION

1.1 Background
Aerosols are solid or liquid particles suspended in a gas. Atmospheric aerosols are a complex mixture of species such as nitrates, sulfates, sea salt, crustal materials, and organic and elemental carbonaceous compounds. Atmospheric aerosol exposure adversely affects human health: PM$_{2.5}$ and PM$_{10}$ (particles with aerodynamic diameter smaller than 2.5 and 10 µm, respectively) is capable of penetrating the respiratory system, settling on lung tissue, and being absorbed into the bloodstream (Donaldson et al., 2001). Many aerosol constituents are carcinogenic, and particulate matter (PM) exposure has been shown to cause respiratory and cardiovascular diseases as well as neurological disorders and depression (Bell et al., 2013; Fonken et al., 2011; Grahame et al., 2014; Mauderly and Chow, 2008; Pope, 2007; Pope and Dockery, 2006).

Atmospheric aerosols drive climate by exerting a radiative forcing, or a net change between the energy entering and leaving the Earth system (Forster et al., 2007). Aerosols absorb or scatter solar radiation, respectively warming or cooling the atmosphere (the “aerosol direct effect”). Aerosols also affect cloud lifetime and albedo by altering the microphysics of nucleation (the “aerosol indirect effect”). Furthermore, warming driven by anthropogenic emissions are having an effect on sea ice, ocean pH, as well as negatively impacting the Atlantic Meridional Overturning Circulation, which could lead to sea level rises. The direct and indirect effects of aerosols contribute the largest uncertainty to the total anthropogenic radiative forcing estimate (IPCC, 2015).

Among the aerosol constituents, it is known that black carbon (BC) or elemental carbon (EC) is a strong solar radiation absorber and causes atmospheric heating (Bond et al., 2013). The climate impact of organic carbon (OC), particularly the light-absorbing brown carbon (BrC), has not been well studied (Andreae and Gelencser, 2006). Accurate measurement of BC, BrC, and OC is essential in reducing the uncertainties in carbonaceous aerosol emission inventory as well as their air quality and climate impacts. BrC and BC have different optical properties and thus exert different radiative forcing effects.
illustrated in Figure 1-1, carbonaceous particle components have a range of spectra in thermochemical refractiveness and optical absorption properties in accordance to their molecular structure. Non-refractory OCs consist of low-molecular weight (MW) hydrocarbons and derivatives do not usually absorb light. Higher MW OCs, such as Polycyclic Aromatic Hydrocarbons (PAHs) and HUmic-LIke Substances (HULIS), are usually refractory, have strong absorption efficiency at shorter wavelengths, and have a brownish appearance, giving them the name of BrC. EC consists of graphite-like material and strongly absorbs light at all wavelength, giving the name of BC. While their differences are recognized, the terms BC and EC are often used interchangeably in the literature.

![Classification of carbonaceous aerosol components based on thermochemical and optical properties as well as molecular structure (Pöschl, 2003).](image)

BC is characterized by light-absorbing carbonaceous species with absorption proportional to $\lambda^{-1}$ (Ångström absorption exponent [AAE] of 1). This occurs because the imaginary part $k$ of the complex refractive index $m (=n+ik$, with $n$ and $k$ being the real and imaginary part of $m$) is nonzero and carries weak wavelength dependence over the visible and near-visible spectrum (Moosmüller et al., 2009). BC monomer particles are small ($< 0.3 \mu m$) and act as volume absorbers – particles that absorb light throughout their volume rather than large particles that act as surface absorbers.
Freshly-emitted BC particles form long-chain fractal aggregates (Kahnert and Devasthale, 2011) that collapse into spherical masses as they age in the atmosphere. These fresh aggregates appear as small particles and thus act as volume absorbers, whereas collapsed aggregates behave more like surface absorbers.

BrC aerosols are light-absorbing organic carbon (OC) aerosols emitted from low-temperature combustion (smoldering) of biomass. Some BrC are secondary organic aerosol (SOA) formed from biogenic or anthropogenic precursors (Jang et al., 2002; Yu et al., 2009). Smoldering combustion is flameless surface oxidation of solid fuel (Gao et al., 2003; Reid et al., 2005). The aerosol emission mechanism during smoldering is distinct from flaming emissions: smoldering emits low-volatility organic compounds (Gao et al., 2003) that rapidly condense into growing particles that may polymerize with OH radicals in water (Reid et al., 2005) resulting in spherical accumulation mode particles (Bergstrom et al., 2007; Dinar et al., 2008; Graber and Rudich, 2006; Hoffer et al., 2006; Kirchstetter et al., 2004; Sun et al., 2007). These aerosols have been shown to absorb short-wavelength solar radiation (Andreae and Gelencser, 2006; Moosmüller et al., 2009). The optical properties of BrC may be due to water-soluble organic compounds, which contain polycyclic aromatic, phenolic, and acidic functional groups (Hoffer et al., 2006; Lee et al., 2014; Nguyen et al., 2013) and humic-like substances (HULIS) (Graber and Rudich, 2006), which can have Ångström exponent $\alpha$ as large as 6-7 (Graber and Rudich, 2006). Atmospheric HULIS have been shown to have markedly different properties than terrestrial or aquatic humic substances. BrC aerosols have imaginary part $k$ that carries a significant wavelength dependence, increasing towards the shorter visible and UV wavelengths, resulting in an absorption Ångström exponent $\alpha$ much larger than 1 (Alexander et al., 2008; Andreae and Gelencser, 2006; Moosmüller et al., 2009). BrC are generally hydrophilic as strong oxidation is involved in the formation processes. This implies stronger CCN activity for BrC and indirect climate effects. Despite the importance of BrC to air quality, climate, and understanding of aerosol source, very little is known about the BrC emission inventory, molecular composition, and optical properties. There is currently no standard method to characterize or quantify BrC (Andreae and Gelencser, 2006; Moosmüller et al., 2009).
Accurate measurement of the optical properties of these aerosols motivates the development of instrumentation capable of a wide spectral range.

1.2 Thermal/Optical Analysis

The Interagency Monitoring of Protected Visual Environments (IMPROVE) network is a federal monitoring network started in 1986 with twenty sites to monitor federal Class 1 areas, primarily national parks and wilderness areas. The IMPROVE network calculates aerosol extinction coefficient with aerosol concentration and speciation data (24 hour samples every third day) (Hand et al., 2013; Malm et al., 1994; Watson, 2002). Some sites monitor optical extinction and scattering with in-situ methods, and photography of a scene is typically taken three times a day. The network has expanded to more than 170 sites since 2000. The samples collected by the IMPROVE network are analyzed for OC and EC at the Environmental Analysis Facility (EAF) of Desert Research Institute (DRI) using single- and multi-wavelength thermal/optical carbon analyzers (DRI, 2012; 2015).

Thermal/optical analysis (TOA) of carbon samples on quartz-fiber filters consists of gradually heating samples through various temperature steps in either a completely inert helium environment or an oxidizing environment of 2% oxygen in helium. Throughout the process, reflectance (R) and transmittance (T) of the filter are monitored. As the sample heats, carbonaceous species is evolved from the filter. It then undergoes different chemical reactions depending on the nature of the detector used. For example, when using a flame ionization detector (FID), the carbon is first oxidized by manganese oxide (MnO$_2$) and reduced to methane (CH$_4$) via a nickel catalyst. If a non-dispersive infrared (NDIR) detector is used, only the oxidation step is required.

A typical ambient sample will contain some mixture of OC and EC. During the inert-environment stage (OC) of thermal analysis, a portion of the organic carbon will be liberated from the filter matrix and be detected by the NDIR, while the rest will pyrolyze, which is the decomposition of a substance by heating to a high temperature. The sample will typically darken as these organic compounds char. This pyrolyzed organic carbon (POC) is considered part of the organic fraction since it was a byproduct of the analysis process, and therefore a portion of measured EC needs to be accounted for in the OC
fraction of analysis (“char correction”). This is known as the OC/EC split. The split point is defined as the point during analysis where an optical signal that monitors the filter returns to the value measured at the beginning of analysis. Everything that evolves before the split is assigned as OC and everything after is assigned as EC. The underlying assumptions for this correction to be valid are either: 1) POC evolves fully before native EC or 2) POC has the same absorption efficiency as EC. Yang and Yu (2002) showed that these assumptions are invalid for many samples. Once the optical signals return to baseline and all POC has been removed from the filter and analyzed, remaining EC is oxidized to carbon dioxide as the sample continues to heat through the remainder of the temperature steps. At the end of the analysis run, a sample of methane calibration gas of known volume and temperature is injected into the instrument.

The data collected by TOA is represented in a time series graph known as a thermogram (Figure 1-2). A thermogram plots temperature, reflectance, transmittance, and NDIR signal peaks. The NDIR peaks are multiplied by the flow rate and integrated and compared to the methane standard peak area to determine the amount of carbon per fraction, while the reflectance and transmittance data are used to determine the split between OC and EC.

Measurement of thermally-resolved OC and EC fractions in aerosol emissions from gasoline- and diesel-powered vehicles enhanced the ability of receptor models to discriminate between these sources (Watson et al., 1994). Carbon fractions have been used for PM source apportionment at urban and remote locations (Liu et al., 2006; Zhao and Hopke, 2004). These fractions have not been optimized around the decomposition temperatures of common aerosol constituents.

Given the importance of BC in global climate (Bond et al., 2004), much effort has been expended on reconciling BC and EC from different measurement protocols (Watson et al., 2005). Inter-laboratory comparison studies show that different thermal methods agree within 5-15% on the total carbon (TC) concentrations, but the EC and OC concentrations can differ by a factor of up to 7, with a common difference by a factor of two (Chow et al., 2004; Schmid et al., 2001; Watson et al., 2005). Therefore, there is an urgent need to reduce EC and OC measurement uncertainties.
The original protocol for Thermal/optical reflectance (TOR) analysis of carbon samples was much different than the IMPROVE_A (Chow et al., 2007) protocol used today. The Oregon Graduate Center Carbon Analyzer (OGC) first investigated thermal/optical carbon analysis and the problem of pyrolysis, incorporating an optical charring correction system (Huntzicker et al., 1982). The OGC process began with a helium purge followed by heating the sample to 350°C in He/O\(_2\) to volatilize OC. The O\(_2\) was then purged by helium and residual OC was volatilized at 600°C in an inert atmosphere. The sample was then cooled to 400°C, and He/O\(_2\) was reintroduced. Remaining EC was volatilized at 400, 500, and 600°C. Then, the sample was cooled to 350°C and the methane calibration standard was injected. All evolved species were oxidized by manganese dioxide (MnO\(_2\)), reduced to CH\(_4\), and analyzed by an FID. A Motorola 6802 microprocessor-based computer gathered all data which was saved to cassette tapes and analyzed by another computer.

The first IMPROVE TOR protocol (Chow et al., 1993a) was developed by a DRI/OGC instrument built at DRI. This protocol consisted of volatilization of OC at 120, 250, 450, and 550°C in an inert helium atmosphere, then combustion of EC at 550, 700, and 800°C.
in a 2% O\textsubscript{2} environment. However, the downstream oxidation, reduction, and detection methods are identical to the OGC.

The IMPROVE\textsubscript{A} protocol (Chow et al., 2007) is the standard analysis protocol used by the U.S. long term IMPROVE network. IMPROVE\textsubscript{A} was developed following more refined measurements of the sample temperature and methods to calibrate the temperature reported by the instrument (Chow et al., 2005). The protocol defines OC steps at 140, 280, 480, and 580°C in an inert helium environment, and EC fractions at 580, 740, and 840°C in an oxidizing 2% O\textsubscript{2}/98% He environment. The downstream oxidation, reduction, and detection methods of the Model 2001 are identical to older methods. In addition to reflectance data, transmittance of laser light through the filter is also monitored.

In addition to the IMPROVE network, the U.S. Environmental Protection Agency operates the PM\textsubscript{2.5} Chemical Speciation Network (CSN). This network was implemented in 2000 and has approximately 180 sites around the United States. The site collects ambient samples on quartz-fiber, Nylon, and Teflon filters, and provides data on total particulate mass; multielemental ions (sulfate, nitrate, ammonium, sodium, and potassium); and OC and EC. Quartz-fiber filters from CSN are analyzed using the IMPROVE\textsubscript{A} protocol.

There are many other regional and global networks around the world, as well as individual Supersites that extensively study atmospheric aerosols with a variety of instrumentation, not necessarily filter-based methods. Examples of other networks include the Global Atmosphere Watch’s GAW Programme, the European Environment Agency’s EuroAirnet, and the CARE-China network, comprised of 36 stations operated by the Chinese Academy of Sciences. Different carbon analysis protocols are used by these networks.

While the IMPROVE\textsubscript{A} is the standard protocol for thermal/optical analysis of carbon samples in U.S. networks, other protocols are also used in other countries. Since OC and EC are operationally defined, different protocols partition them differently. For example, the NIOSH protocol agrees with the IMPROVE\textsubscript{A} protocol for total carbon, but NIOSH usually reports less EC than IMPROVE\textsubscript{A} (Chow et al., 2001).
1.3 Overview of this Research

Thermal/optical analysis is an important tool for studying and quantifying visibility, air quality, receptor modeling and source apportionment, all of which contribute to air quality legislation, emissions inventories, and climate modeling. However, the so-called “intensive properties” (Andrews et al., 2011) of aerosols such as aerosol single scattering albedo ($\omega$), Ångström exponent ($\alpha$), hemispherical backscatter fraction ($\beta$), and asymmetry parameter ($g$) are wavelength dependent, independent of particulate concentration. These parameters, in particular the Ångström exponent, can help characterize different carbonaceous species as OC, BrC, or EC. It is therefore desirable to examine the thermal evolution of aerosol compounds under multiple wavelengths. To that end, a modern thermal/optical carbon analyzer was developed. This research addresses the following objectives:

1) Design and construct a modernized thermal/optical carbon analyzer with multiwavelength capabilities.

Previous thermal/optical instruments (such as the DRI Model 2001 Carbon Analyzer) have used single-wavelength measurements for char correction. Other instruments, such as a 7-wavelength Aethalometer (Arnott et al., 2005; Hansen et al., 1984), operate at multiple wavelengths but do not differentiate carbonaceous particles by thermal properties. This new instrument, the DRI Model 2015 Multiwavelength Carbon Analyzer (referred to as Model 2015 in this thesis), operates on the same thermal protocols as previous thermal/optical instruments while monitoring optical reflectance (R) and transmittance (T) at 405, 445, 532, 635, 780, 808, and 980 nm. To modernize the design, off-the-shelf components were emphasized over proprietary components, with the only exception being two printed circuit boards, one for modulating the light source and acquiring the optical signals and the other for holding the transmittance photodiode. However, these circuit boards are designed to be easily replicated to ensure future availability.

2) Characterize the Model 2015 Multiwavelength Carbon Analyzer to establish equivalency to legacy analyzers and determine operational parameters.

To establish equivalency between the Model 2015 and the legacy Model 2001, several hundred archived samples collected from the Fresno Supersite (Chow et al., 2009; Park et
al., 2006; Watson et al., 2000) and the IMPROVE network were analyzed by both instruments. Quantities of TC, as well as OC and EC fractions were compared with char correction using 633 nm and 635 nm by Models 2001 and 2015, respectively.

To infer the absolute R and T from the Model 2015 optical signal, transfer standards were generated using filters of different PM loading and color (including Fresno ambient PM, diesel exhaust, and combustion exhaust of pine needles, pine cones, and peat) and characterized by a UV-VIS spectrometer (PerkinElmer Lambda 35). The absolute R and T can be used to infer wavelength-dependent absorption efficiency, and to estimate light absorption by BrC and BC.

The Model 2015 performance specifications such as minimum detection limit (MDL) and highest quantifiable limit (HQL) were investigated, as well as the linearity of the detector’s response.

3) **Apply the Model 2015 Multiwavelength Carbon Analyzer to ambient and source samples to investigate the wavelength dependence of the OC/EC split and the absorption efficiencies of EC and POC.**

Thermal analysis suffers from an uncertainty in the partitioning of OC and EC due to pyrolysis, which is the charring of species in an inert atmosphere at high temperatures. POC is assumed to behave optically like EC at 635 nm, i.e., they have the same absorption cross section ($\sigma$). However, this assumption is invalid (Yang and Yu, 2002) and raises the question: is there a wavelength where $\sigma_{POC} \approx \sigma_{EC}$? The results of this question could lead to better choice of wavelength for char correction.

4) **Demonstrate the Model 2015 Multiwavelength Carbon Analyzer’s ability to perform different thermal protocols.**

The IMPROVE_A thermal/optical protocol (Chow et al., 2007; Chow et al., 2011) has been adopted by the IMPROVE network and U.S. EPA CSN as the standard protocol for OC and EC measurements. Other protocols, such as NIOSH (Birch and Cary, 1996), EPA STN (Peterson and Richards, 2002) and EUSAAR_2 (Cavalli et al., 2010) are also used in other applications or networks. Since OC and EC are operationally defined, the reported values
often vary by the protocol used. Each of these protocols has a different OC4 temperature plateau, which has been shown to have an effect on EC measurement (Subramanian et al., 2006). This study investigates the comparability between IMPROVE_A, NIOSH, EUSAAR_2, and STN protocols along with the wavelength-dependence of reported OC and EC. Both reflectance and transmittance analyses were performed.
2 DESIGN OF THE DRI MODEL 2015 MULTIWAVELENGTH CARBON ANALYZER

2.1 Motivation

The DRI Model 2015 Multiwavelength Carbon Analyzer (Model 2015) was developed to investigate the wavelength-dependent nature of BC and BrC while simultaneously being comparable with legacy instruments (i.e., Model 2001) to maintain consistency with current OC and EC analysis protocols for long-term network monitoring. The Model 2015 was developed with the following criteria:

- Establish equivalence to Model 2001 while running the IMPROVE_A protocol (Chow et al., 2007; 2011) at nearest available wavelength (635 nm for Model 2015, 633 nm for Model 2001) (Chen et al., 2015b; Chow et al., 2015).
- Add multiwavelength optical monitoring
- Ensure stable and reliable performance
- Facilitate ease of construction, operation, and maintenance
- Use a minimum of proprietary components, focusing on readily available off-the-shelf components.
- Reduce construction and operation cost.
- Emphasize on computer control over manual control of components and parameters.
- Reduce physical footprint.

These requirements are necessary to ensure that the Model 2015 can operate reliably and consistently for long periods of time. The Model 2001 has been in continuous service since it was developed in 2000, in many cases being operated around the clock for weeks to months at a time. However, the Model 2001 is facing an impending end-of-life milestone, as many proprietary components are no longer being manufactured. By choosing off-the-shelf components and a minimum of proprietary parts (which are easily reproduced), the Model 2015 can be expected to last many years.
A standalone upgrade was developed concurrently with Model 2015 in order to add multiwavelength capabilities to existing Model 2001 analyzers. This device consists of a seven-wavelength light source, 8-furcated optical fiber, data acquisition card, and a circuit board responsible for modulating the lasers, acquiring and conditioning reflectance and transmittance sensor data, and communicating the results to a LabView program. The LabView program is a separate process running alongside Model 2001 “DRICarb” software, which was modified to take data from the LabView program and incorporate it into thermograms. The design of the retrofit is discussed briefly in Section 7.2.

2.2 Principle of Operation

Thermal/optical carbon analysis is based on the preferential oxidation of OC and EC materials under different temperatures and atmospheres (Watson et al., 2005). Its function relies on the fact that organic compounds can be volatilized from the sample deposit in a non-oxidizing helium (He) atmosphere, while EC must be combusted with an oxidizer. Figures 2.1a and 2.1b show a mechanical overview of the major components in Model 2015. Figure 2.2 shows photographs of the instrument. Figure 2.3 shows the light source and detectors (Chen et al., 2015b; Chow et al., 2015), and Figure 2.4 details the sample analysis region.
Figure 2-1: Schematic diagrams of the upper (a) and lower (b) sections of the Model 2015.
Figure 2-2: Photographs of the instrument. Top: the instrument with cover on. Bottom: analyzer interior showing sample loading hardware, temperature controllers, and sample cooling fan.
Figure 2-2 continued. Top: instrument interior showing NDIR, six-port injector valve, and solenoid valves. Bottom: solenoid valves.
Figure 2-2 continued. Top: the coupling of the fiber optic cable and the quartz cross oven. Bottom: sample analysis region showing heating blocks and septum injection port.
The Model 2015 operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (~0.5 cm\(^2\)) taken from a quartz-fiber filter or other sample forms; 2) converting these compounds to carbon dioxide (CO\(_2\)) by passing the volatilized compounds through an oxidizer (heated MnO\(_2\)); 3) quantifying the CO\(_2\) by a NDIR CO\(_2\) detector.

The analysis procedure begins when a quartz-fiber filter sample is loaded into a quartz boat, which is then mechanically moved into the analysis region by a stepper motor. Limit switches along the path report the sample’s position to the computer. Once the sample passes deep enough into the quartz cross oven, valves toggle the flow of pneumatic air to close a breech and seal the oven. The cross oven is pressurized at ~35 kPa, which is monitored to ensure the oven is sealed. Inert carrier gas (99.9999% ultrapure helium) fills
and purges the oven while the sample continues moving into analysis position, seated between quartz light rods in the heating chamber. The temperature is held stable between 45°C and 50°C for twenty seconds, and baselines are acquired for NDIR CO₂, reflectance, and transmittance signals. Once the background signals are accepted by the computer, analysis begins by heating to the first temperature step (OC1) specified in the analysis protocol. The computer advances to the next fraction after a pre-determined amount of time, or in the case of the IMPROVE_A protocol once the NDIR signal returns to baseline, whichever comes first. After OC4 ends (current published protocols only have four OC fractions), solenoid valves toggle to introduce 2% O₂ (EC1 fraction) to the sample to combust POC and EC. Analysis continues through the remaining EC fractions and ends with a calibration gas injection. The computer program then integrates the product of NDIR concentration and total flow rate to determine the amount of carbon per fraction. The integration takes into account the transit time, which is the time it takes for the analyte to pass from the filter to the NDIR.

Seven modulated diode lasers measure the reflectance from and transmittance through each filter sample at wavelengths from 405 to 980 nm. The 635 nm laser maintains constancy with the DRI Model 2001, which uses a helium-neon 632.8 nm wavelength laser to correct for pyrolysis charring of OC compounds into EC. Without this correction, the OC fraction of the sample might be underestimated and the EC fraction might include some POC. The correction for pyrolysis is made by continuously monitoring the sample R and T throughout an analysis cycle. The R and T, largely dominated by the presence of light absorbing EC, decrease as pyrolysis takes place and increase as light-absorbing carbon is liberated during the later part of the analysis. By monitoring the R and T, the portion of the EC peak corresponding to POC can be accurately assigned to the OC fraction. The correction for the charring conversion of OC to EC is essential for a less-biased measurement of carbon fractions (Johnson et al., 1981). The Thermal Optical Reflectance (TOR) and Thermal Optical Transmittance (TOT) charring corrections are not necessarily the same, owing to charring of organic vapors adsorbed within the quartz fiber filter (Chen et al., 2004; Chow et al., 2004). Traditionally, charring is only monitored by one red laser. The multiwavelength R and T monitoring provides an opportunity to systematically study
charring under different wavelengths and potentially improve the charring correction accuracy.

Carbonate carbon can be determined by measuring the CO$_2$ evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions (i.e., OC1-4 and EC1-3), as well as the 7-wavelength TOR and TOT charring correction, are individually quantified and reported when the IMPROVE_A (Chow et al., 2007; 2011) temperature protocol is applied. Values routinely reported include seven-wavelength total OC, total EC, TC (sum of total OC and total EC), and pyrolyzed carbon, monitored by both reflectance (OPR) and transmittance (OPT). Depending on the thermal/optical protocol applied for quantification, thermally-derived sub-fractions of OC and EC, and carbonate carbon, are reported.

*The particular operation procedure for the Model 2015 at Desert Research Institute is covered in detail in the Model 2015 Multiwavelength Carbon Analyzer Standard Operating Procedure (DRI, 2015).*

### 2.3 Instrument Design

#### 2.3.1 Addressing the Design Criteria

During the design process, the criteria stated in Section 2.1 were approached holistically. In some cases, some trial and error was required before determining the best approach to the problem. Here the challenges and solutions of each point are investigated. Table 2-1 lists the major differences between the Models 2001 and 2015. The frame and machined components were designed in Dassault Systèmes SolidWorks and manufactured by a local metalworking shop. The image and text on the front of the case was designed in Adobe Photoshop and printed by a local vinyl graphics company.
Table 2-1: List of key design differences between Models 2001 and 2015.

<table>
<thead>
<tr>
<th>Component</th>
<th>Model 2001</th>
<th>Model 2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Source</td>
<td>632.8 nm He-Ne laser</td>
<td>405, 445, 532, 635, 780, 808, and 980 nm diode lasers</td>
</tr>
<tr>
<td>Fiber optic</td>
<td>Bifurcate fibers (bundle)</td>
<td>8-furcated fibers (single)</td>
</tr>
<tr>
<td>Sample oven</td>
<td>One arm outlet to detector</td>
<td>Branched side-arm with He/O₂ inlet</td>
</tr>
<tr>
<td>Flow control</td>
<td>Manual Rotameters</td>
<td>Mass flow controllers</td>
</tr>
<tr>
<td>Sample oven Power Supply</td>
<td>24 VAC</td>
<td>24 VDC</td>
</tr>
<tr>
<td>Temperature controllers</td>
<td>Analog Watlow temperature controllers</td>
<td>Digital Watlow temperature controllers</td>
</tr>
<tr>
<td>Standard injection</td>
<td>Custom-made Carle valve</td>
<td>Valco 6-port injection valve</td>
</tr>
<tr>
<td>Circuit boards</td>
<td>Multiple custom proprietary boards</td>
<td>One generic programmable board and one photodiode holder</td>
</tr>
<tr>
<td>Carbon detector</td>
<td>Flame ionization (CH₄) detector (requires ultrapure H₂)</td>
<td>NDIR (CO₂) detector (no H₂)</td>
</tr>
<tr>
<td>Conversion after thermal evolution</td>
<td>Oxidation (to CO₂) and reduction (to CH₄)</td>
<td>Oxidation (to CO₂)</td>
</tr>
<tr>
<td>Data acquisition</td>
<td>Keithley</td>
<td>National Instruments</td>
</tr>
<tr>
<td>Software</td>
<td>Visual Basic/C++</td>
<td>LabVIEW</td>
</tr>
</tbody>
</table>

**Multiwavelength Optical Monitoring**

Figure 2-4 compares the optical design of the Models 2001 and 2015. The Model 2001 uses a 633 nm helium-neon (He-Ne) laser as the light source. The laser is mechanically modulated by an optical chopper modulated at 60 Hz, and uses a lock-in amplifier to reduce noise. Bifurcate bundled optical fibers introduce the incident light to the quartz light pipe, and bring the reflectance signal back to the photodiode detector. Optical filters are placed
in front the photodiodes to only allow a narrow wavelength range centered at 633 nm (±5 nm) to be detected, thereby reducing interference from stray light, particularly that due to glow of the sample oven. The Model 2015 uses seven diode lasers (405, 445, 532, 635, 780, 808, and 980 nm) as the light source. The lasers are modulated at 30 Hz and sequentially turned on one at a time for two pulses per laser. Eight-furcated single optical fibers transmit the incidence and reflectance light. The laser modulation and signal recovery are described in more detail in Section 2.3.3.1.

![Figure 2-4](image.png)

**Figure 2-4.** Optical configurations for: a) Model 2001; and b) Model 2015. Mechanical modulation of the 633 nm helium-neon (He-Ne) laser is replaced by sequential pulse modulation of seven diode lasers. The aerosol deposit faces the incident radiation in both cases. The single optical fiber in the Model 2015 provides more efficient light transmission than the optical fiber bundle in the Model 2001.

**Equivalence to Model 2001 while running the IMPROVE_A protocol at nearest available wavelength (635 nm for Model 2015, 633 nm for Model 2001):** To ensure that the chemical and physical principles of the established methods of thermal/optical analysis are consistent when using the Model 2015, some elements of the Model 2001 analyzer were retained. In particular, the sample loading region, optical path, and heating element configuration are largely the same.
A minimum of proprietary components, focusing on readily available off-the-shelf components: Model 2001 utilized a number of complicated proprietary components, particularly circuit boards used to control sample loading, oven temperature, phase-sensitive detection of laser signals, power distribution, and flow rates. The capabilities of modern, readily available components obviate the creation of proprietary components, and the Model 2015 was designed to take advantage of this.

A National Instruments (Austin, TX) data acquisition system (NI-DAQ, PCIe-6341) replaces the Keithley KPCI-3102A, which is no longer manufactured. The NI-DAQ’s digital and analog inputs and outputs control much of the system from software, rather than relying on hardware-based methods. The hardware-based lock-in amplification of laser signals was replaced by laser modulation and digital signal processing, which is discussed in Section 2.3.3.

Internal power supplies have been replaced with DC power supplies at 24V/600W for the sample heater, 12V/150W for valve and flow controllers, and 3.3V/25W for the lasers (TDK-Lambda SWS-600, LS150-12, and LS25-3.3, respectively). Updating the power supplies carries a number of advantages. The power supplies chosen for the Model 2015 are fully-enclosed switching DC power supplies with features such as short circuit protection and computer-controlled on/off (SWS-600 only). A DC sample oven power supply eliminates noise from the optical sensors from the AC oscillations in the heating coils. 12- and 3.3-volt supplies are compact and inexpensive with sufficient power output for all components.

The mechanical action has been updated to a commercially-available stepper motor and controller board (AutomationDirect STP-MTR-23055, STP-DRV-4035), while the thermocouple push rod and breech pistons are identical to Model 2001. The laser lock-in amplification and optical signal recovery circuits were replaced with a single printed circuit board. The transmittance photodiode board is a printed circuit board, however its design is easily replicated. Mechanical rotameters were replaced with computer-controlled mass flow controllers and meters (Alicat M-1SLPM-D-SV/5M, M-1SLPM-D/5M), and the flame ionization detector was replaced with a NDIR detector (PP Systems AGA407).
Temperature controllers were updated to modern proportional-integral-derivative (PID) controllers with digital computer interface (Watlow STKA-AHAK-AAA). The custom six-port injection valve was replaced with a six-port injection valve with standard 1 mL sample loop and heater block (Valco ED26UWE, SL1KCW, HA1). The heater block is controlled by a microcontroller (Arduino Nano 3.1) running a simple feedback control loop. The purpose of the heater block is to maintain the standard injection sample at a constant temperature so that injection mass is independent of room temperatures and consistent between analyses. Reflectance and transmittance photodiodes have been updated to Thorlabs (Newton, NJ) silicon photodiodes (FDS100 and FDS010, respectively).

**Simplified operation and maintenance, needing fewer reagents:** In the Model 2001 analyzer, an FID measures methane concentration. This methane is produced from carbonaceous species on the filter by a two-step process, each requiring a different reactor. The first is an MnO$_2$ reactor that oxidizes carbon to CO$_2$, and the second is a nickel nitrate catalyst reactor that reduces CO$_2$ to methane ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$). In the Model 2015, the NDIR detector is capable of measuring CO$_2$ directly and no methanator (and therefore no ultrapure hydrogen nor nickel catalyst) is required. In Model 2001, there is no oxygen passing through the MnO$_2$ oxidation oven during the OC analysis stage. Even if not all carbonaceous species were oxidized by MnO$_2$, they would be reduced to CH$_4$ and detected by the FID. Since the NDIR is only sensitive to CO$_2$, it would not detect all carbon if they were not 100% fully oxidized to CO$_2$. To ensure complete conversion of evolved carbon to CO$_2$, the oxidation oven was updated from the Model 2001 from a single-bulb (Figure 2-5) to a double-bulb configuration with side-arm injection of carrier gas (Figure 2-6).
Figure 2-5: Model 2001 quartz cross with a single-bulb oxidation oven shown (shaded region).

Figure 2-6: Model 2015 with quartz cross with a double-bulb oxidation oven (shaded region). The presence of O₂ in both OC and EC analysis stage as well as the larger volume of MnO₂ ensure conversion of carbon to CO₂. Volume shown is the total volume of the catalyst.

**Emphasis on computer control over manual control of components and parameters:**

While the second design goal stated that components needed to be updated to off-the-shelf alternatives, it was also emphasized that these components be able to interface with the LabView software via the NI-DAQ. This reduces the risk of accidentally altering an important operating parameter and affecting analysis results. Furthermore, computer
control allows more parameters to be logged to the database, resulting in better quality control, troubleshooting, and repair.

**Ease of construction and maintenance:** Model 2001 is a complicated analog instrument, despite the data acquisition interface with a computer. Cables and tubing are routed in a way that makes them nearly inaccessible, while circuit boards and other components are wedged between hot oven enclosures and the instrument frame with little clearance for maintenance. This makes troubleshooting and maintenance difficult.

Effort was made to compartmentalize major components of the Model 2015. As shown in Figures 2-1 and 2-2, electrical and flow components are kept separated except where necessary, and the instrument is separated into two major sections. The lower section of the instrument houses behind-the-scenes components such as power supplies, mass flow controllers, 6-port injection valve controller, desiccant/CO₂ scrubber, relays, breakers, power distribution, and the NI-DAQ breakout box (SCB-68a). The upper section contains the analysis hardware, such as the seven-wavelength light source and printed circuit board, quartz oven cross, sample loading motor and breech, heater controllers, NDIR, and sample oven fan. Various needle valves control the sample oven pressure and the leak check valve recovery regulator. In short, hardware that a laboratory technician needs regular access to is located in the top section.

The lower and upper sections are assembled separately and then brought together and all interconnections are made via either flexible Teflon tubing or by passing connection cables through holes in the upper platform. Plumbing interconnects are made via bulkheads (Swagelok B-200-61) while electrical cables are protected by various rubber grommets.

For maintenance, the Model 2015 is designed such that when the lid is removed, the instrument is fully accessible from all sides. Cables and plumbing are routed to be easy to follow in case an electrical or flow diagnostic is needed, all components are clearly labeled, and no esoteric tools are required for maintenance.

**Smaller physical footprint:** The Model 2015 was designed to take up less space on a laboratory bench by utilizing the two-tier design. This update reduces the footprint from
0.6 m² to 0.4 m². Early designs tried to incorporate the host PC into the analyzer, but this was dismissed as being overly complex.

2.3.2 Prototyping with 3D Printers

With the proliferation of consumer-grade 3D-printers, prototyping components has become streamlined and inexpensive, and with appropriate design, 3D-printers can also generate custom parts with sufficient quality for production. These parts would normally cost thousands of dollars to manufacture with traditional methods, and may in fact be impossible to create. Using MakerBot Replicator 2 and Replicator 2X 3D-printers, several parts (Figure 2-7) were created for use in the Model 2015.

To create a compact light source module housing all seven wavelengths as well as the reflectance sensor (Figure 2-7e), a part was designed in SolidWorks to accommodate the various diameters of the lasers. The file was then imported into software to prepare files for 3D-printing. It was then built from acrylonitrile butadiene styrene (ABS) plastic using appropriate parameters to ensure ruggedness and opacity. 3D-printing is not a perfect technology, and the printed part still needs to be inspected to make sure the lasers fit, and then it must be tapped to accept ¼”-32 SMA adapters, the standard adapter for fiber optic connectors. Optionally, a part printed from ABS may be smoothed in an acetone vapor bath, though this is primarily for aesthetic purposes.

By utilizing 3D-printing, difficult parts that would take weeks to create in a traditional machine shop can be ready to install in the Model 2015 within hours. By keeping the entire process in-house, any parameter of the part can be modified (for example, if a new laser manufacturer is chosen and the dimensions of the laser holder need to be changed).

In addition to the 7-wavelength light source holder, other parts were created to hold the sample oven blower fan (Figure 2-7a) and the onboard desiccator for makeup flow (Figure 2-7b). A small holder for the reflectance photodiode was made from polylactic acid (PLA) plastic (Figure 2-7c), and a bracket to hold the 8-furcate cable bundle was made from ABS (Figure 2-7d).
Figure 2-7: Plastic parts 3D-printed for the Model 2015 (pictures not to scale): a) Sample oven fan holder; b) CO\textsubscript{2} scrubber holders; c) reflectance photodiode holder; d) bracket for 8-furcated fiber optic cable, and e) laser holder and cover.
If another laboratory with a Model 2015 requires a part, they can either print it themselves on a 3D printer or order from a number of online vendors specializing in 3D printing, such as Shapeways.

2.3.3 Design of the Seven-Wavelength Optical System

2.3.3.1 Laser Modulation and Signal Recovery

Different approaches to laser modulation and recovery were investigated before settling on a serial pulse train with reference signal. A xenon lamp and spectrometer arrangement was initially used to extract continuous multiwavelength data, though this approach was problematic due to overwhelming data and the inability to distinguish between the xenon lamp and the thermal glow of the oven coils. The high cost of the xenon lamp and spectrometer as well as the short lifespan (~1000 hours) of the lamp are also undesirable. Instead of a continuous xenon spectrum, discreet diode lasers at seven wavelengths (405, 445, 532, 635, 780, 808, and 980 nm) were chosen. The advantages of lasers are that a wide range of intensities are available, their lifespan (~5000 hours) is much longer than the xenon lamp, they are easily modulated, and the cost is relatively low. Originally, each laser was simultaneously modulated at different coprime frequencies and the data were extracted via Fourier analysis. This approach involved significant hardware and software overhead. Finally, a serial “pulse train” method was investigated, with lasers being pulsed sequentially, twice each at 30 Hz. These pulses arrive simultaneously with a reference transistor-transistor logic (TTL) signal (5V hardware output, scaled to ±1V by the LabView software) modulated at the same frequency (Figure 2-8). The reference signal is multiplied by the laser signals, and the result is integrated over each laser’s two pulses to determine the extracted signal (Chen et al., 2015b). This approach is beneficial in that it cancels most systematic noise due to electromagnetic interference from mains power or other ambient electrical noise. To discriminate between individual cycles and synchronize the laser modulation and signal integration, a marker pulse is triggered at the beginning of the first laser pulse and remains at logical high for the duration of an entire pulse train.
Since the multiwavelength light source makes the use of a notch filter on the photodiodes impossible, a subtracting amplifier along with a software algorithm is used to keep the transmittance signal within the detectable range.

![Diagram](image)

**Figure 2-8:** Arrangement of light source, detectors, and modulation/extraction algorithm.

### 2.3.3.2 Design of the Laser Control Circuit Board

The hardware that governs the seven wavelength laser source modulation and signal recovery is the only proprietary electronic component in the Model 2015. Its functions are: 1) modulate the seven lasers and output reference and marker signals, and 2) interface with the reflectance and transmittance photodiodes, acquiring their signals, and amplifying them before passing them to the NI-DAQ.

This board underwent several revisions between 2013 and 2015. Early versions used eight individual microcontrollers (Arduino Nano 3.1) in a star network configuration with a central microcontroller distributing triggering signals to seven others, each responsible for modulating a single laser. Lasers were controlled by modulating a Darlington transistor with a logic signal, which in turn actuated a solid-state relay (Crydom CN024D05) that
controlled power to the lasers (Figure 2-9a). The disadvantages of this design were the excess Arduinos and lack of a unified system to acquire laser signals.

The design of the circuit board improved incrementally. Streamlined code allowed the eight individual microcontrollers to be replaced with a single Arduino Nano. The first printed circuit board (Version 1, Figure 2-9b) included a two-channel amplifier (Burr-Brown OPA2277) for the optical signals. This amplifier is recommended by National Instruments for optical signals for its fast slew rate (maximum rate of change of output), rail-to-rail operation, and high gain-bandwidth product. It is powered by a ±12V power supply (TDK-Lambda CC1R5-1212DF-E) installed directly on the PCB. The next revision (Version 2.0, Figure 2-9c) saw the inclusion of the 3-stage amplifier for the transmittance detector, packaged in a single IC with the reflectance amplifier (Burr-Brown OPA4277); however the laser actuation circuitry was identical to the first prototype. Blue indicator LEDs were also included which fire simultaneously with the lasers. These LEDs can help diagnose where in the system a failure may be occurring if a particular laser is not working.

The next revision (Version 3.0, Figure 2-9d) was the second major revision, marked by an emphasis on miniaturization, inclusion of safety features, and the move away from prefabricated microcontroller breakout boards (the Arduino) to an onboard Atmel MEGA328P microcontroller, programmed directly by Future Technology Devices International (FTDI) interface. The cumbersome transistor-relay combination was replaced with a dual-output high-side load switch (Texas Instruments TPS27081A) for each laser. This was the major step towards miniaturization. While still a 4-layer board, the majority of components were replaced with surface-mount packages and the connectors were miniaturized (Molex PicoBlade). This design performed quite well, although constructing miniature connectors by hand in the laboratory soon became inefficient and unreliable.

Version 4.0 (Figure 2-9e) retained all the features of Version 3.0 while emphasizing usability over miniaturization. The FTDI interface was replaced with in-circuit serial programming (ICSP) to better facilitate bootloading and programming, and the PicoBlade connectors were replaced with Molex MicroBlade, which are slightly larger and easier to work with. Manual control was first added in this revision, allowing a technician to activate
the lasers without needing input from the PC. This board was paired with a new circuit for
the photodiodes, which included an active amplifier (Burr-Brown OPA227) rather than a
passive Ohm’s Law amplifier. Unfortunately, this board did not perform as well as previous
versions, introducing excessive noise to the optical signals. This was attributed to changing
the design to a two-layer board and contracting with an inferior fabrication house (ITEAD
Studios).

Version 5.0 (Figure 2-9f) re-introduced the circuit design proven by Version 3.0 and avoids
the flaws of Version 4.0 by returning to ExpressPCB as the manufacturer. Additional safety
features were incorporated to ensure that lasers cannot errantly fire by floating signals on
the logic lines. An identical Version 6.0 (Figure 2-9g) has superseded Version 5.0, but is a
complete turnkey solution, requiring no in-house assembly. It was designed in KiCad (an
open-source Eagle variant designed and maintained by the European Organization for
Nuclear Research) and manufactured by Bittele Electronics, Incorporated (Toronto,
Canada). By providing laboratories with the information and files necessary to order this
board themselves, a new board can be acquired from any reliable turnkey production house,
essentially future-proofing the only proprietary component of the Model 2015.
a) Arduinos Nano 3.1

Darlington NPN transistors
b) Transistor-relay combination

Single-stage amplifier

c) Multiple-stage amplifier
d) Surface-mount multiple-stage amplifier

Onboard microcontroller

Load switches
Figure 2-9a-g: The laser control board design iterations.
2.4 Instrument Setup and Calibration

Calibration procedures are discussed in detail in the Model 2015 Multiwavelength Carbon Analyzer Standard Operating Procedure (DRI, 2015). Optical calibration and equivalence are discussed in Section 3.2.

2.4.1 Optical Power Adjustment and Oven Glow Mitigation

The diode lasers at the chosen wavelengths are typically available in a discrete selection of power levels, and the available power levels vary greatly for different wavelength. For example, the 635 nm laser is available at 30 mW while the 808 nm laser is available at up to 150 mW. The current selections of laser power are: 405 nm – 100 mW; 445 nm – 80 mW; 532 nm – 30 mW; 635 nm – 30 mW; 780 nm – 120 mW; 808 nm – 150 mW; and 980 nm – 60 mW.

These choices aim to have sufficient and relatively uniform reflectance and transmittance signals across all wavelengths, with the wavelength sensitivity function of the photodiodes are taken in to account. Some lasers (e.g., 780 nm) are typically available in relatively high powers, and the reflectance and transmittance photodiodes have slightly different sensitivity functions. These lasers can saturate the detectors even at low amplification. To adjust the laser signals so that the detector response is reasonably uniform at all wavelengths, neutral density filters (Kodak Wratten) are placed in front of lasers that saturate the detector until they are within the detection range of the photodiode circuits and roughly as intense as some of the weaker lasers.

As described earlier, the Model 2001 utilized a single wavelength HeNe laser and lock-in amplification to produce excellent signal-to-noise ratio. Furthermore, since a single wavelength is used, an optical bandpass filter (632±5 nm) ensures that only the laser signal makes it through to the reflectance and transmittance sensors. The Model 2015’s multiwavelength light source requires a different arrangement, and oven glow can saturate the photodiodes at high temperatures when blackbody radiation is significant at wavelengths that the detectors are sensitive to.

A number of steps are employed to mitigate this oven glow problem. The inner surfaces of the oven firebrick enclosure are painted with a high-temperature black paint to absorb some
of the glow. The sample oven power supply was replaced with a 24V/600W direct current (DC) supply to suppress AC oscillation being picked up by the optical sensors. While heating, the laser signal uniformly increases due to oven glow fast enough so that the baseline reading between individual laser pulses changes. The laser signal recovery algorithm was modified to account for this. The printed circuit board contains a three-stage amplifier for the transmittance detector. The first stage is available to a technician to modify the amplification with a potentiometer in the place of the feedback resistor. The second stage is a subtracting amplifier that takes as its non-inverting input the amplified photodiode signal, while the inverting input is a signal provided by the NI-DAQ’s analog output. This signal is derived from the photodiode signal when the lasers are off, and therefore mostly generated by the oven glow. This baseline adjustment is applied dynamically to account for the baseline increase due to oven glow in real time. With appropriate choice of resistors ($R_{\text{potentiometer}}$, $R_{\text{ground}} = 1k\Omega$), the amplification function then becomes

$$V_{\text{out}} = 2 \cdot V_{PD} \left( \frac{R_{\text{potentiometer}}}{R_{\text{ground}}} \right) - V_{\text{DAQ}}$$

(2-1)

so that the final signal seen by the NI-DAQ has a constant DC offset to pull the signal down below the saturation threshold at all times (see Section 7.1, Appendix I – Electrical for schematic). This does not affect the signal extraction algorithm. The third stage is a unity-gain buffer amplifier to make a clean, zero-impedance signal available to the NI-DAQ.

To make sure that R and T signals will not saturate (exceeding 10 V) during the entire analysis, a blank filter is placed in the sample oven. R and T of all lasers are adjusted to 1-5 V at room temperature. 1V is the minimum acceptable signal for good signal-to-noise ratio. Next, the sample oven is heated from 50 to 840ºC, and the R and T signals are monitored during the temperature increase. The potentiometers are adjusted so that the R and T for the highest laser signal are close to 8 V to avoid saturation while achieving good signal-to-noise ratio.
2.4.2 Thermal Calibration and Optimization

Since the thermocouple tip of the sample pushrod is a few millimeters away from the actual sample, temperature calibration is required so that the thermocouple temperatures represent the actual temperature of the sample. Temperature standards are prepared by coating the top surface of a quartz fiber filter punch with Tempilaq° G, a substance that changes color at a specific temperature. Tempilaq° G is available at 44 different indicating temperatures. For calibration, temperatures of 121, 184, 253, 510, 704, and 816°C are used (Chow et al., 2005; 2007). The second-order derivative of reflectance and transmittance are plotted with temperature, and the inflection point of the optical signals is the point at which the desired temperature is attained. The target temperature as measured by reflectance is often approximately 0-2°C lower than the target temperature as measured by transmittance. Since Tempilaq° G is guaranteed to be accurate to within ±1% of the nominal temperature, the average of the reflectance and transmittance targets is used.

The Tempilaq° G calibration has been a standard practice (DRI Model 2001 SOP) because it represents the actual temperature of the filter sample. However, this method is very time consuming and will contaminate the quartz oven which has to be replaced after calibration. Different temperature calibration methods are being investigated, one of them by using a NIST-certified thermocouple. For this method, the fiber optic bundle is removed from the top of the quartz oven, and the light rod is removed. With a blank filter in the sample boat, the NIST thermocouple is then inserted through the upper optical arm and positioned so that the tip is just touching the filter. Several temperatures are set with the computer, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 300, 360, 420, 480, 540, 580, 680, 740, and 840°C. These temperatures span the IMPROVE_A protocol and provide sufficient data points such that the calibration curve is reliable.

For both methods, the requested temperature is plotted against the actual temperature. A linear regression is computed. For the NIST thermocouple method, two separate regressions are computed, one for temperatures below approximately 300°C and one for temperatures above. This is to compensate for differences in heating rates at low and high temperatures. Preliminary tests on a few analyzers show that these two methods yield
similar calibration curves, as shown in Figure 2-10. In this example, the two curves are $y_{NIST} = 1.0168x - 0.4498 \ (r^2=0.9998)$ and $y_{Tempilaq} = 1.0386x + 12.161 \ (r^2=0.9996)$. Typically, curves generated by both NIST and Tempilaq methods are quite close, though more tests are needed to confidently establish their equivalency.

After calibration is completed, the instrument software runs an automatic temperature optimization routine which fine-tunes the parameters used to quickly and accurately adjust to the different fraction temperatures so the oven does not significantly overshoot a target temperature, as this may inadvertently desorb carbon belonging to a higher-temperature fraction.

![NIST and Tempilaq Calibration Curves](image)

**Figure 2-10:** Comparison of NIST and Tempilaq methods from calibration of a Model 2015.

### 2.4.3 Mass Flow Calibration

Figure 2-11 shows the flow diagram of the Model 2015. Four mass flow controllers (MFC) are used to control the helium, helium/oxygen, and NDIR makeup air flow into the system, and a mass flow meter (MFM) is used to measure the total flow through the NDIR. These MFCs and MFM must be calibrated to measure flow under standard conditions (at 20 °C and 101.3 kPa). They are first calibrated during initial setup and then annually, or whenever a flow imbalance is noticed. An external reference flowmeter (i.e., DryCal) with a range of 5-500 mL/min is used to measure the volumetric flow through the mass flow controllers and meter. Standard flow is determined from the relationship
\[ Q_{\text{standard}} = Q_{\text{DryCal}} \times \left( \frac{MFC \text{ Pressure}}{\text{Standard Pressure}} \right) \times \left( \frac{\text{Standard Temperature}}{MFC \text{ Temperature}} \right) \]  \hspace{1cm} (2-2)

As with the temperature calibration, the measured flowrates are plotted against the mass flow controller/meter set points, and a linear regression is used to obtain the calibration equations for each device. The user then inputs these values into software.

Figure 2-11: Pneumatic diagram of Model 2015 Carbon Analyzer. Numbers on the diagram represent the flow at that point and are in mL/min. The large orange region represents the double-bulb MnO\(_2\) reactor showing He2 or He/O\(_2\) injected into the center.

Because the mass flow readings depend on the gas composition, they need be calibrated with the same gas composition when they are used in carbon analysis. Once properly calibrated, the NDIR flow rate should be equal to the sum of He-1, He-2, He/O\(_2\), and makeup flows. If not, either the calibration was unsuccessful or there is a leak in the system.

2.4.4 Carbon Calibration

The carbon calibration for the carbon analyzers are of three types: 1) the routine beginning and end-of-day calibration injections of He/CH\(_4\) and He/CO\(_2\); 2) the end-of-run CH\(_4\) internal calibration peak; and 3) full carbon calibration, performed every six months, using
potassium hydrogen phthalate (KHP), sucrose, CH₄, and CO₂. The procedure to calibrate the Model 2015 for normal use is identical to the procedure for the Model 2001. Standard solutions of 1800 ppm carbon sucrose and KHP are prepared or acquired. Then, a series of blank filters are loaded with 5, 10, 15, and 20 µL and analyzed with the IMPROVE_A protocol. A series of gas injections at the septum port are also analyzed with a special gas analysis protocol. Injections are 200, 500, 700, and 1000 µL of CO₂ and CH₄. If any of the data points are outliers, that particular standard may be re-analyzed. A calibration curve is obtained by plotting the number of µg carbon in the standard against the normalized integrated signal from the NDIR.

Figures 2-12a and b show an example carbon calibration from CA#17.

![Figure 2-12a: Example carbon calibration with individual standards identified.](image)
Figure 2-12b: The same graph as Figure 2-12a with linear regression drawn through the points. The slope and intercept are then programmed in to the software.

Calibration procedures are described in detail in the Model 2015 Multiwavelength Carbon Analyzer Standard Operating Procedure (DRI, 2015).

2.5 Summary

A new thermal/optical carbon analyzer with multiwavelength capabilities was designed, developed, and calibrated per the Model 2015 Standard Operating Procedure (DRI, 2015). By focusing on key design goals, the Model 2015 is a robust and reliable laboratory instrument with an emphasis on off-the-shelf components and a powerful software package capable of handling most of the instrument’s operation. The machined parts and sheet metal were designed in SolidWorks and a local metalworking shop manufactured them. 3D-printing was used to manufacture certain parts quickly and inexpensively, including the laser module holder, sample oven fan holder, and other components.
3 CHARACTERIZATION OF THE MODEL 2015
MULTIWAVELENGTH CARBON ANALYZER

This chapter describes the characterization the Model 2015 minimum detection limit (MDL), upper detection limit (UDL), the linear range of the NDIR, and the optical calibration with transfer standards.

3.1 Detection limits

The Model 2015 measurement range is bracketed by the MDL and UDL. MDL was determined via analysis of 100 blank laboratory samples, while UQL was back-calculated from the NDIR’s stated maximum 2000 ppm limit and tested with high concentrations of sucrose calibration solutions. The lower quantifiable limit (LQL) is determined from field blanks and is therefore unique for individual measurement projects and is not quantified here. LQL can be lowered by quality control detailed in the Standard Operating Procedures for both Model 2001 and 2015 (DRI, 2012, 2015).

3.1.1 Minimum detection limit

MDL is defined as three times the standard deviation of the measured results of the laboratory blanks. Data were controlled for errors in measurement indicated by negative peak areas, as well as excessively high peak areas (>1 µg carbon) which indicate that the filter may have been contaminated. MDLs are reported at each wavelength for both reflectance and transmittance. The MDLs calculated are:

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>OCR (µg/cm²)</th>
<th>OCT (µg/cm²)</th>
<th>ECR (µg/cm²)</th>
<th>ECT (µg/cm²)</th>
<th>TC (µg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>405</td>
<td>0.14 ± 0.05</td>
<td>0.15 ± 0.05</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>445</td>
<td>0.17 ± 0.06</td>
<td>0.16 ± 0.05</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>532</td>
<td>0.13 ± 0.04</td>
<td>0.13 ± 0.04</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>635</td>
<td>0.18 ± 0.06</td>
<td>0.15 ± 0.05</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td>0.18 ± 0.06</td>
</tr>
<tr>
<td>780</td>
<td>0.17 ± 0.06</td>
<td>0.20 ± 0.07</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>808</td>
<td>0.17 ± 0.06</td>
<td>0.19 ± 0.06</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>980</td>
<td>0.17 ± 0.06</td>
<td>0.17 ± 0.06</td>
<td>0.04 ± 0.01</td>
<td>0.05 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>
These figures vary slightly from the MDL of Model 2001 (0.43, 0.12, and 0.49 μg/cm² carbon per OC, EC, and TC respectively). Using the 635 nm laser to compare, MDL for OCR (TOR reported by IMPROVE_A) has improved by 0.25 μg/cm² while MDL for ECR has improved by 0.08 μg/cm². TC has improved by 0.31 μg/cm².

3.1.2 Upper detection limit and Linear Range

The NDIR CO₂ detector is specified to measure a maximum of 2,000 ppm CO₂. However, the specified maximum of commercial detectors is often understated. The design of the Model 2015 is such that 200 standard mL/min of flow is delivered to the NDIR throughout analysis, which at 2000 ppm CO₂ is a maximum detectable CO₂ rate of 400 μL/min. Under the assumption that 2000 ppm CO₂ is the maximum, at standard conditions (i.e., 101.3 kPa and 20 °C), the maximum detectable carbon flow rate is 3.35 μgC/sec.

Several custom standards were created to test the linear range and observe the behavior of the Model 2015 at high carbon flow rates. Preparations of 12.5, 5000, and 100000 (nominal; 12.3, 5000.4, and 99876.7 actual concentration by gravimetric analysis) ppm carbon (ppmC) sucrose calibration standard in addition to the common 1800 ppmC standard solution used for routine calibration and testing were analyzed by the Model 2015 in aliquots of 5, 10, 15, and 20 μL each. This corresponds to a test range of 0.062 – 1999.25 μgC per punch, or 0.12 – 3998.5 μgC/cm² when using a punch size of 0.5 cm². Several tests were conducted at each of the four concentrations, with extra data points obtained from the 12.5 ppmC solution to better characterize the behavior of the instrument near the MDL.

The Model 2015 showed good linearity from ~0.2 to ~10000 μgC/cm² (Figure 3-1). Below its detection limit of 0.48 μgC/cm², data show more scattering and deviate from the 1:1 line, differing from actual carbon by up to 165%. Despite this, r² for the entire test was 0.996.

During the 5000 and 100000 ppmC tests, OC3 fraction peaks (reported in ppm CO₂) were observed to far exceed the stated limit of the NDIR while still reporting TC accurately to within 1-12%. For example (Figure 3-3), the 10 μL aliquot of 100000 ppmC sucrose solution was measured by the Model 2015 to contain 978.8 μgC (within 2% of actual) and
the NDIR peak reached nearly 12000 ppm CO$_2$. The 20 µl aliquot was within 12% of actual carbon content and the NDIR peak reached ~21500 ppm CO$_2$.

Taking the 15 µl aliquot of 100000 ppmC sucrose as a maximum (since 20 µl begin to deviate slightly) practical limit, the UQL can be estimated to be approximately 1500 µgC per punch, which corresponds to ~3000 µgC per cm$^2$.

![Sucrose Standards for Linearity](image)

Figure 3-1: Linearity tests with sucrose standards. Strong correlation with the 1:1 line is observed over several decades, while below the MDL results deviate. R$^2$ for the regression is 0.996. Axes are logarithmic, the blue line is the 1:1 line, and the black dotted line is the least-squares regression line.

The linearity of the Model 2001’s FID was tested for comparison. The FID performs well at low concentrations, with a slope of 1.024 when linear regression is performed on 12.5 ppC and 1800 ppmC. However, at high concentrations the FID error is approximately 20%. Linear regression slope of all points is 0.77.
Figure 3-2: Linearity test of the FID with the same standards from the NDIR test.

Figure 3-3: Thermogram of 10 µl aliquot of 100000ppm solution. The OC3 peak nearly reaches 12000 ppm CO₂, far above the manufacturer's stated 2000 ppm range.
3.2 Calibration of Reflectance and Transmittance Signals

The Model 2015 measures laser reflectance and transmittance (denoted as LR and LT, respectively) in 7 wavelengths during the entire analysis. LR and LT at the beginning of the thermal analysis represent light attenuated by the filter and particle, while LR and LT at the end of thermal analysis represent light attenuated by the filter since the light absorbing carbon is removed in the thermal analysis. By taking the ratio of the initial to final LR and LT, the light absorption properties for each sample can be estimated. For example, (Chen et al., 2012) used the LR and LT attenuations at 633 nm of the Model 2001 to demonstrate a consistent decreasing EC trend in the IMPROVE network during 2000-2009. The 7 wavelengths measurement by the Model 2015 will allow estimation of the wavelength-dependent light absorption coefficient \( b_{abs} \). Given the large number of samples per year analyzed by TOA worldwide, the optical data acquired as part of the analysis could be used, in addition to OC and EC, for studies relevant to source apportionment, human health, visibility, and climate (Chen et al., 2015b; Chow et al., 2015).

The optical data analysis is analogous to the principle of optical absorption monitors such as integrating plate/sphere analyzer (Campbell et al., 1995; Chow et al., 2010), the aethalometer (Hansen et al., 1984), particle-soot absorption photometer (PSAP) (Bond et al., 1999; Virkkula et al., 2005; 2010), and the multi-angle absorption photometer (MAAP) (Petzold and Schönlinner, 2004). Both the aethalometer and PSAP apply transmittance attenuation while the MAAP incorporates both reflectance and transmittance attenuations in the calculation of \( b_{abs} \). Black carbon (BC) concentrations can be derived from \( b_{abs} \) by applying a mass- and wavelength-specific absorption efficiency (MAE\( _\lambda \), typically in \( \text{m}^2/\text{g} \)).

The multi-wavelength aethalometer and PSAP have revealed different spectral patterns that are indicative of BC, BrC, dust, and their mixtures (Favez et al., 2009; Sandradewi et al., 2008a; Virkkula et al., 2005; Yang et al., 2009). All these instruments need to compensate for multiple scattering and loading effects of the particle-filter matrix that causes deviations from the simple Beer’s Law (Arnott et al., 2005; Chen et al., 2004; Drinovec et al., 2015; Virkkula, 2010).
LR and LT from Model 2015 are relative but not absolute quantities, because their values depend on not only optical properties of the sample but also laser intensity, photodiode response function, and the optical components arrangement (Chen et al., 2015b). Therefore, LR and LT are different for different analyzers, and will be different even for the same analyzer if the optical components are changed. To make LR and LT comparable among different instruments or different instrument setup and to obtain the most information from the multiwavelength measurements, absolute reflectance and transmittance from the filter (FR and FT, respectively) is desired. This is accomplished by using transfer standards composed of increasing aerosol deposits on quartz-fiber filters identical to those used for routine sampling. Absolute FR and FT (in % of incident light) were determined by an integrating-sphere spectrometer (Lambda 35, Perkin Elmer, Massachusetts, USA (Zhong and Jang, 2011) tracable to the National Institute of Standard and Technology for wavelengths between 300 and 1000 nm.

Figure 3-4 illustrates five sets of optical transfer filter standard types (i.e., Fresno ambient PM$_{2.5}$, diesel exhaust, flaming pine needle, smoldering peat, and smoldering pine cone) used in this study (Chow et al., 2015), each set containing nine filters from blank to heavily loaded with particles. The Fresno ambient PM$_{2.5}$ samples were acquired using high-volume samplers from the Fresno Supersite (Chow et al., 2009; Park et al., 2006; Watson et al., 2000), with EC loadings ranging from 0.9 to 15.8 µg/cm$^2$. The high-volume sampler (filter size of 406 cm$^2$) represent well-characterized urban aerosol while providing sufficient sample for extensive testing.
Figure 3-4: Optical transfer standard filter samples used in this study. The far left sample is the blank from each batch.

The source samples were prepared from laboratory-generated aerosols using a diesel generator, flaming dry pine needles, smoldering damp pine cones, and smoldering Florida peat (Chow et al., 2015). Diesel exhaust was generated by an Onan Cummins 12.5 kW diesel generator with an accumulated 2,500 hours operating on commercial diesel fuel (<15 ppmw sulfur content) under idling conditions. Biomass samples were combusted in a Pineridge Genuine Woodstove. Dry Sierra Nevada pine needles (recovered from the forest floor) were ignited with a butane lighter and sampled only during the flaming phase. Sierra Nevada pine cones were wetted with water and subjected to a temperature-adjustable electric heater to a flameless smoldering prior to sampling. Florida peat was also ignited by the electric heater to a smoldering phase. Samples were drawn from the plume of each source through a Bendix 240 PM$_{2.5}$ cyclone at a total flow rate of 113 L/min into a conical mixing chamber (Chow et al., 1993b). The cyclone inlet was placed at ~ 0.5–1.5 m from the emission point to allow for cooling and dilution with ambient air and to obtain a wide range of deposit opacities. Eight pre-fired 47 mm quartz-fiber filters and two Teflon-membrane filters were mounted to the 12-port manifold with Savillex FEP Teflon filter holders. Flow rates through the filters ranged from 1 and 32 L/min, in a logarithmic sequence, to obtain increasing deposits on each filter. A DustTrak DRX (Wang et al., 2009)
monitored particle concentrations in real time to adjust sample durations, which ranged from ~5 min for diesel exhaust to 15 min for peat smoldering. This yielded aerosol deposits ranging from ~0.05–1.5 mg/filter. Filters were weighed before and after sampling to determine the amount of aerosol collected.

Figure 3-4 shows that the diesel and flaming standards are similar in appearance to many ambient samples, with shades changing from light gray to deep black. The smoldering standards have a yellowish-brown appearance that is distinct from the others. Figure 3-5 plots the absolute FR and FT measured by the UV/VIS spectrometer for the five sets of transfer standards in Figure 3-4. Similar to their visual appearance, the FR and FT shapes are separated into two groups: 1) Fresno, diesel, and flaming pine needles (grey-black); and 2) smoldering peat and pine cone (yellowish). The FR and FT curves for the second group are much steeper than the first groups, indicating much stronger light absorption with decreasing wavelength, consistent with greater AAE for brown carbon. The curves for the first group are flatter, indicating relatively uniform light absorption across the wavelength.

Each transfer standard was placed into the Model 2015 and Model 2001 sample boat and inserted into the analysis zone to measure instrument-specific LR and LT for one or two minutes to obtain an average photodiode detector response. The detector output is linear over several decades, and it responds to different wavelengths at both high and low R and T values, so the outputs are scaled such that they can be viewed on a similar basis. The optical calibration curves of LR and LT vs. FR and FT are plotted in Figure 3-6.

Based on the calibration curves, absolute FR and FT in % can be inferred from carbon analyzer photodiode LR and LT signals. Atmospheric absorption coefficient as a function of wavelength, \( b_{\text{abs}}(\lambda) \), for the integrated filter deposit can then be estimated from attenuations (ATN) in either the absolute filter R or T, defined by:

\[
\text{ATN}_R(\lambda) = \ln\left(\frac{FR(\lambda)_{\text{final}}}{FR(\lambda)_{\text{initial}}}\right) \quad (3-1)
\]

\[
\text{ATN}_T(\lambda) = \ln\left(\frac{FT(\lambda)_{\text{final}}}{FT(\lambda)_{\text{initial}}}\right) \quad (3-2)
\]
where $FR(\lambda)/FT(\lambda)_{initial}$ and $FR(\lambda)/FT(\lambda)_{final}$ are the time-averaged (typically 10 seconds) initial and final filter reflectance/transmittances at each wavelength, respectively. Although the $FR(\lambda)_{final}$ and $FT(\lambda)_{final}$ may differ from those of a true blank filter due to refractory residues after the thermal analysis, the ratio of final over initial FR and FT represents the attenuation by the particles evolved during the analysis. In the first-order approximation (Hansen et al., 1984; ISO, 1993; Lindberg et al., 1999; Quincey, 2007), $b_{abs}(\lambda)$ of the thermally liberated fraction including OC and EC can be expressed as:

$$b_{abs}(\lambda) \cong ATN_R(\lambda) \times \left(\frac{A}{2V}\right)/100$$  \hspace{1cm} (3-3)

$$b_{abs}(\lambda) \cong ATN_T(\lambda) \times \left(\frac{A}{V}\right)/100$$  \hspace{1cm} (3-4)

where $A$ is the area (cm$^2$) of the surface deposit and $V$ is the sample volume (m$^3$). These yield $b_{abs}(\lambda)$ in the commonly used unit of inverse megameter (Mm$^{-1}$) (Richards, 1984; Watson, 2002). The comparison of $b_{abs}(\lambda)$ by R and T will be discussed in Chapter 4.
Figure 3-5: Optical calibration of transfer standard samples determined with a calibrated UV/VIS spectrophotometer. Sample loadings increase for higher-numbered samples. Vertical lines designate the seven wavelengths in Model 2015.
e) Pine Needle Reflectance
f) Pine Needle Transmittance

f) Peat Reflectance
g) Peat Transmittance

h) Pine Cone Reflectance
i) Pine Cone Transmittance

Figure 3-5 continued.
Figure 3-6: Reflectance (a and b) and transmittance (c and d) calibration curves derived from LR and LT by Model 2015 (a and c) and Model 2001 (b and d) and FR and FT by Lambda UV/VIS spectrometer. The laser signals are a constant factor of millivolt photodetector outputs normalized to a common scale for all wavelengths. The factors for Model 2015 and Model 2001 are different due to their different optical setup.
3.3 Equivalence between Model 2015 and Model 2001

The Interagency Monitoring of PROtected Visual Environments (IMPROVE, 2015) thermal/optical carbon analysis protocol (Chow et al., 1993a; 2007; 2011) has been consistently applied at the non-urban IMPROVE and urban Chemical Speciation Network (CSN, U.S.EPA, 2015) sites since 1986 and 2005/2006, respectively, thereby allowing long-term trends to be assessed (Chen et al., 2012; Murphy et al., 2011). Consistent trends are needed to develop emission control strategies in urban areas and track reasonable progress toward natural visibility conditions by CY 2065 at U.S. national parks and wilderness areas, as required by the Clean Air Visibility Rule (U.S.EPA, 1999; U.S.EPA, 2005; Watson, 2002). Figure 3-7 shows these trends at a representative site from the IMPROVE network, indicating that emission reduction measures are having a positive effect on lowering ambient concentrations. In addition to the IMPROVE and CSN networks, the IMPROVE protocol has been adopted for other long-term PM chemical speciation networks in the U.S. (Hansen et al., 2006), Canada (Dabek-Zlotorzynska et al., 2011), and China (Huang et al., 2012; Zhang et al., 2012), as well as for shorter-term ambient and source characterization studies in these and other parts of the world. Since OC and EC are operationally defined by the measurement protocol, changes in equipment and procedures may adversely affect the ability to track trends. As shown in Figure 3-7, a small increase in EC and a small decrease in OC is observed in 2005, which may have been attributed in part to the replacement of the DRI/OGC carbon analyzers by Model 2001 in that year. However, this feature was not consistent at all of the IMPROVE sites that underwent the same change (Chen et al., 2012). This illustrates some of the difficulties in changing instrumentation and methods in assessing trends, and highlights the critical importance of maintaining equivalency when the analyzer or method changes. As discussed in Chapter 2, maintaining equivalency between Models 2015 and 2001 is a fundamental design goal, and rigorous testing has been carried to ensure the equivalency. The equivalency between Models 2015 and 2001 are demonstrated in two steps: 1) a batch of samples are analyzed with the IMPROVE_A protocol on Models 2001 and 2015 to demonstrate comparable precision, and 2) A batch of same filters are analyzed in both Models 2001 and 2015.
Figure 3-7. Trends in annual average organic carbon (OC) and elemental carbon (EC) concentrations at the Shenandoah National Park IMPROVE site. The red line indicates the year (CY 2005) when the Model 2001 thermal/optical carbon analyzer replaced the DRI/OGC carbon analyzers. Data were obtained from CIRA (2014).

Figure 3-8 shows the comparisons of replicate sample carbon data on Model 2001 (left panels) and Model 2015 (right panels). These samples are from the collocated PM$_{2.5}$ samplers (X-Module) in the IMPROVE network. Because only three 0.5 cm$^2$ punches can be taken from these 25 mm diameter filters, the two batches analyzed in Model 2001 and Model 2015 had different filters, each containing 17 samples. The two analyses on each model were run more than one month apart, so the analyzer set up may have changed between runs but all analyzers passed quality control assessment during the analyses.

Figure 3-8 shows that both models have excellent measurement precision for TC, OC and EC by reflectance (i.e., OCR, ECR) and transmittance (i.e., OCT, and ECT) with the Deming regression slopes (Deming, 1943) within two standard errors ($\pm 2 \sigma$) of unity. The carbon fractions (i.e., OC1-OC4, EC1-EC3, OPR, and OPT) slopes are still close to 1 but deviate more from unity, ranging from 0.88$\pm$0.20 to 1.05$\pm$0.02 for Model 2001 and 0.88$\pm$0.04 to 1.07$\pm$0.03 for Model 2015, respectively. It is expected that the thermal fractions are not as precise as TC, OC, and EC because they are very sensitive to the sample oven temperature, trace level O$_2$ in the analyzer, sample inhomogeneity, and semi-volatile OC adsorption, desorption, and transformation (Chow et al., 2007; 2015). However, the precision of Models 2001 and 2015 are comparable for these replicate samples.

Both the Models 2001 and 2015 analyzers were used to analyze the same ambient PM samples to further demonstrate equivalency. These samples include 71 filters from the non-urban IMPROVE network collected during 2010-2013, 73 filters from the IMPROVE
collocated X-Module samplers collected during 2010-2014, and 67 filters from the Fresno supersite collected during 2003-2005. Figure 3-9 compares the TC, OC, EC, and carbon fractions between the Model 2001 and 2015 analyzers. The statistical comparisons of the three groups along with the total number of 221 samples are listed in Table 3-2. As expected, TC is equivalent, with the averages agreeing within ±5% and regression slopes (m) ranging from 0.93 and 1.01 for all three sub-groups and the overall samples. The relative difference (RD), defined as the ratio of the difference divided by the average of two measurements on the same sample, varies from -1±19% to 3±17%. OC and EC, either by reflectance or transmittance are also statistically equivalent, with slope within 1.00±0.05 for most comparison groups. The IMPROVE X-Module and IMPROVE samples showed higher RD and lower R² for ECR and ECT, mainly due to the lower level of EC in these non-urban sites. ECR is higher than ECT, consistent with previous studies (Chow et al., 2001; Schmid et al., 2001). Similar to the observations in the replicate samples (Figure 3-8), the carbon faction data have more spread, with slope varying from 0.67 to 1.32. This variability is typical of that among replicates from different carbon analyzers as reported by Chow et al. (2007). One of the inter-instrumental variabilities was attributed to temperature calibration, which could deviate up to ±1% from the specified values (Chow et al., 2005; 2015). As a result, the error bars for carbon fractions are larger than those for TC, OC, and EC, although most of them still include the 1:1 line (Figure 3-9). In addition, some OC species (particularly OC1) are semi-volatile and can undergo desorption, adsorption, and transformation during the storage period. OC1 is always found to be poorly reproduced even in replicates analyzed on the same instrument as shown in Figure 3-8. Figure 3-10 compares OCR and ECR from two IMPROVE sampling periods (2005-2009 vs. 2010-2013). While the EC slopes are comparable, the OC from the 2005-2009 period shows lower slope (0.84) than those from the 2010-2013 period (slope = 0.95), indicating losses of some OC in the archive.
Figure 3-8. Replicate analyses of IMPROVE (x-module) samples (N = 17) on Model 2001 (left panels) and Model 2015 (right panels). OC1, OC2, OC3, and OC4 are organic carbon evolved at 140, 280, 480, and 580 °C, respectively, in a 100% He atmosphere. EC1, EC2, and EC3 are elemental carbon evolved at 580, 740, and 840 °C, respectively, in a 98% He / 2% O2 atmosphere. OP is pyrolyzed organic carbon by reflectance (OPR) or transmittance (OPT). OCR = (OC1 + OC2 + OC3 + OC4) + OPR. OCT = (OC1 + OC2 + OC3 + OC4) + OPT. ECR = (EC1 + EC2 + EC3) – OPR. ECRT= (EC1 + EC2 + EC3) – OPT. TC = OC + EC.
Figure 3-8 continued.
Figure 3-8 continued.
Figure 3-8 continued.
Figure 3-8 continued.
Figure 3-9: Comparison of Models 2001 and 2015 for Fresno (n = 67), IMPROVE (n = 71), and IMPROVE X modules (n = 73) samples.
Figure 3-9 continued.

OC2 Model 2015 (µg/cm²) vs. OC2 Model 2001 (µg/cm²)

- Slope = 1.00 ± 0.05
- R² = 0.97

EC1 Model 2015 vs. EC1 Model 2001

- Slope = 0.84 ± 0.01
- R² = 0.97

OPR Model 2015 vs. OPR Model 2001

- Slope = 0.77 ± 0.04
- R² = 0.76

EC2 Model 2015 vs. EC2 Model 2001

- Slope = 1.18 ± 0.04
- R² = 0.71

OPT Model 2015 vs. OPT Model 2001

- Slope = 0.80 ± 0.02
- R² = 0.92
Table 3-2: Comparison of Fresno, IMPROVE, and IMPROVE X modules samples measured by the Models 2001 and 2015 following the IMPROVE_A protocol (x is Model 2001 and y is Model 2015).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sample # and Average (µg/cm²)</th>
<th>Correlation Coefficient</th>
<th>Deming Regression y = m × x</th>
<th>Relative Difference (y-x)/(y+x)/2</th>
<th>Mean ± 1σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresno</td>
<td>67 23.76 24.18</td>
<td>0.99</td>
<td>1.01 ± 0.01</td>
<td>0.02 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>IMPROVE X</td>
<td>73 8.04 7.83</td>
<td>0.96</td>
<td>0.97 ± 0.01</td>
<td>-0.01 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>IMPROVE</td>
<td>71 13.65 13.07</td>
<td>0.99</td>
<td>0.93 ± 0.03</td>
<td>0.03 ± 0.17</td>
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</tr>
<tr>
<td>Overall</td>
<td>211 14.92 14.79</td>
<td>0.99</td>
<td>0.97 ± 0.02</td>
<td>0.01 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>OCR</td>
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<td></td>
</tr>
<tr>
<td>Fresno</td>
<td>67 18.68 19.30</td>
<td>0.99</td>
<td>1.03 ± 0.01</td>
<td>0.04 ± 0.07</td>
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</tr>
<tr>
<td>IMPROVE X</td>
<td>73 6.88 6.72</td>
<td>0.95</td>
<td>0.97 ± 0.01</td>
<td>-0.01 ± 0.20</td>
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<td>IMPROVE</td>
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<td>0.99</td>
<td>0.93 ± 0.03</td>
<td>0.04 ± 0.18</td>
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<tr>
<td>Overall</td>
<td>211 12.43 12.41</td>
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<td>0.97 ± 0.02</td>
<td>0.02 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>OCT</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresno</td>
<td>67 20.98 21.23</td>
<td>0.99</td>
<td>1.00 ± 0.01</td>
<td>0.02 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>IMPROVE X</td>
<td>73 7.36 7.20</td>
<td>0.96</td>
<td>0.97 ± 0.01</td>
<td>0.00 ± 0.19</td>
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</tr>
<tr>
<td>IMPROVE</td>
<td>71 12.86 12.40</td>
<td>0.99</td>
<td>0.93 ± 0.03</td>
<td>0.04 ± 0.17</td>
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</tr>
<tr>
<td>Overall</td>
<td>211 13.53 13.40</td>
<td>0.99</td>
<td>0.97 ± 0.02</td>
<td>0.02 ± 0.15</td>
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</tr>
<tr>
<td>ECR</td>
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<td></td>
</tr>
<tr>
<td>Fresno</td>
<td>67 5.08 4.88</td>
<td>0.97</td>
<td>0.95 ± 0.02</td>
<td>-0.03 ± 0.14</td>
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</tr>
<tr>
<td>IMPROVE X</td>
<td>73 1.16 1.11</td>
<td>0.94</td>
<td>0.98 ± 0.03</td>
<td>-0.19 ± 1.04</td>
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<td>IMPROVE</td>
<td>71 1.42 1.31</td>
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<td>0.96 ± 0.04</td>
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</tr>
<tr>
<td>Overall</td>
<td>211 2.49 2.37</td>
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<td>0.95 ± 0.02</td>
<td>-0.20 ± 0.79</td>
<td></td>
</tr>
<tr>
<td>ECT</td>
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<td></td>
<td></td>
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<tr>
<td>Fresno</td>
<td>67 2.78 2.96</td>
<td>0.96</td>
<td>1.08 ± 0.02</td>
<td>0.04 ± 0.17</td>
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</tr>
<tr>
<td>IMPROVE X</td>
<td>73 0.69 0.63</td>
<td>0.89</td>
<td>0.95 ± 0.03</td>
<td>-0.30 ± 0.69</td>
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<tr>
<td>IMPROVE</td>
<td>71 0.79 0.73</td>
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<td>0.89 ± 0.04</td>
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<tr>
<td>Overall</td>
<td>211 1.39 1.38</td>
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<td>1.05 ± 0.02</td>
<td>-0.29 ± 0.69</td>
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</tr>
<tr>
<td>OC1</td>
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<tr>
<td>Fresno</td>
<td>67 2.90 1.92</td>
<td>0.94</td>
<td>0.75 ± 0.04</td>
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<tr>
<td>IMPROVE X</td>
<td>73 0.24 0.19</td>
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<td>IMPROVE</td>
<td>71 0.69 0.73</td>
<td>0.98</td>
<td>1.23 ± 0.67</td>
<td>0.37 ± 1.16</td>
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<tr>
<td>Overall</td>
<td>211 1.24 0.92</td>
<td>0.92</td>
<td>1.00 ± 0.25</td>
<td>0.01 ± 1.05</td>
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<tr>
<td>OC2</td>
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<tr>
<td>Fresno</td>
<td>67 4.14 4.59</td>
<td>0.93</td>
<td>1.10 ± 0.02</td>
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<tr>
<td>IMPROVE X</td>
<td>73 1.57 1.52</td>
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<tr>
<td>IMPROVE</td>
<td>71 3.20 3.16</td>
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<td>0.95 ± 0.06</td>
<td>0.06 ± 0.20</td>
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</tr>
<tr>
<td>Overall</td>
<td>211 2.93 3.05</td>
<td>0.97</td>
<td>1.00 ± 0.05</td>
<td>0.05 ± 0.17</td>
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Table 3-2. continued.

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<th>Samples</th>
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<th>Correlation Coefficient</th>
<th>Deming Regression $y = m \times x$</th>
<th>Relative Difference $(y-x)/(y+x)/2$</th>
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<td></td>
<td>$n$ $\bar{x}$ $\bar{y}$ $R^2$ Slope ± 1σ Mean ± 1σ</td>
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<td>Fresno</td>
<td>67 5.99 6.72 0.94 1.14 ± 0.02 0.09 ± 0.13</td>
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<tr>
<td>IMPROVE X</td>
<td>73 4.01 3.71 0.94 0.91 ± 0.08 -0.07 ± 0.27</td>
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<tr>
<td>IMPROVE</td>
<td>71 2.20 2.03 0.87 0.92 ± 0.02 -0.08 ± 0.26</td>
<td></td>
<td></td>
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<tr>
<td><strong>Overall</strong></td>
<td><strong>211 4.01 4.09 0.93 1.02 ± 0.05 -0.02 ± 0.24</strong></td>
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<tr>
<td>OC4</td>
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<tr>
<td>Fresno</td>
<td>67 3.18 4.02 0.93 1.29 ± 0.04 0.22 ± 0.15</td>
<td></td>
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<tr>
<td>IMPROVE X</td>
<td>73 1.25 1.30 0.86 1.05 ± 0.04 0.00 ± 0.32</td>
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<tr>
<td>IMPROVE</td>
<td>71 2.08 2.18 0.98 1.06 ± 0.02 0.07 ± 0.38</td>
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<tr>
<td><strong>Overall</strong></td>
<td><strong>211 2.14 2.46 0.95 1.18 ± 0.03 0.09 ± 0.32</strong></td>
<td></td>
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<tr>
<td>EC1</td>
<td></td>
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<tr>
<td>Fresno</td>
<td>67 7.01 6.17 0.97 0.85 ± 0.01 -0.07 ± 0.14</td>
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<tr>
<td>IMPROVE X</td>
<td>73 2.34 2.27 0.96 0.94 ± 0.02 0.03 ± 0.31</td>
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<tr>
<td>IMPROVE</td>
<td>71 3.17 2.72 0.96 0.77 ± 0.03 0.09 ± 0.48</td>
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<tr>
<td><strong>Overall</strong></td>
<td><strong>211 4.10 3.66 0.97 0.84 ± 0.01 0.02 ± 0.35</strong></td>
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<td>EC2</td>
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<tr>
<td>Fresno</td>
<td>67 0.55 0.73 0.58 1.32 ± 0.05 0.28 ± 0.21</td>
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<td>IMPROVE X</td>
<td>73 0.49 0.54 0.73 1.05 ± 0.09 0.18 ± 0.73</td>
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<tr>
<td>IMPROVE</td>
<td>71 0.43 0.51 0.79 1.18 ± 0.04 0.21 ± 0.64</td>
<td></td>
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</tr>
<tr>
<td><strong>Overall</strong></td>
<td><strong>211 0.49 0.59 0.71 1.18 ± 0.04 0.22 ± 0.58</strong></td>
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</tr>
<tr>
<td>OPR</td>
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</tr>
<tr>
<td>Fresno</td>
<td>67 2.48 2.03 0.25 0.74 ± 0.06 -0.11 ± 0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IMPROVE X</td>
<td>73 1.61 1.68 0.88 0.99 ± 0.05 0.23 ± 0.53</td>
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<td></td>
</tr>
<tr>
<td>IMPROVE</td>
<td>71 2.25 1.97 0.87 0.71 ± 0.05 0.25 ± 0.64</td>
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</tr>
<tr>
<td><strong>Overall</strong></td>
<td><strong>211 2.10 1.89 0.76 0.77 ± 0.04 0.13 ± 0.60</strong></td>
<td></td>
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<tr>
<td>OPT</td>
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<tr>
<td>Fresno</td>
<td>67 4.78 3.96 0.87 0.78 ± 0.03 -0.10 ± 0.24</td>
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<td></td>
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</tr>
<tr>
<td>IMPROVE X</td>
<td>73 2.08 2.15 0.95 0.99 ± 0.03 0.14 ± 0.39</td>
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<td></td>
</tr>
<tr>
<td>IMPROVE</td>
<td>71 2.88 2.61 0.94 0.77 ± 0.04 0.21 ± 0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Overall</strong></td>
<td><strong>211 3.21 2.88 0.92 0.80 ± 0.02 0.09 ± 0.48</strong></td>
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</tr>
</tbody>
</table>
3.4 Summary

The Model 2015 was characterized to determine operating parameters such as MDL, UQL, detector linearity, and the behavior of the optical systems. MDLs for OC, EC, and TC at 635 nm TOR are 0.18, 0.04, and 0.18 μg/cm², respectively. UQL is ~3000 μgC/cm², which far exceeds any realistic loading of a filter sample. The NDIR was found to be linear across several orders of magnitude from 0.1 to 10000 μg/cm², though above 3000 μg/cm² measured carbon deviated by 12% from actual carbon.

LR and LT were calibrated with optical transfer standards composed of ambient and source samples with a wide range of loading. A PerkinElmer Lambda 35 spectrometer measured absolute FR and FT. LR and LT vs. FR and FT were plotted to determine calibration curves so that absolute FR and FT from Model 2015 can be inferred.

Finally, equivalence to legacy Model 2001 carbon analyzer was demonstrated in order to maintain consistency with long-term trend analysis networks (e.g., IMPROVE). Replicate analysis of Fresno and IMPROVE samples on the Model 2015 compared well with legacy Model 2001.
4 APPLICATION OF THE DRI MODEL 2015
MULTIWAVELENGTH CARBON ANALYZER TO AMBIENT SAMPLES

Research Objective 3, stated in Section 1.3, concerns the utility of multiwavelength data to investigate optical properties of BrC, BC, and POC, while Research Objective 4 investigates the differences in the OC/EC split of different thermal protocols based on multiwavelength data. This chapter focuses on application of the Model 2015 to ambient and source samples to investigate how to use multi-wavelength data to partition POC and EC, as well as the OC/EC split reported by the seven wavelengths when the analyzer uses protocols such as NIOSH, STN, and EUSAAR_2. With the array of wavelengths available in the Model 2015, absorption efficiencies of ambient samples were investigated to determine if there is a wavelength such that the absorption efficiencies of EC and POC are more similar than at 632.8 nm that is used in Model 2001.

 Archived Fresno samples were analyzed to investigate the optical properties of EC and POC. Five initial samples from the Fresno Supersite were selected for preliminary protocol comparison, with fifteen more identified for future comparisons to form a statistically-significant analysis.

4.1 Wavelength Dependence and Consistency of the OC/EC Split

As stated previously, the OC/EC split is the point during analysis where an optical signal returns to its pre-analysis value, or baseline. This signifies that POC has been liberated from the filter and native EC has begun to evolve.

Reflectance (R) and transmittance (T) signals both have a split point, and often differ since R is dominated by POC on the filter surface, while T is sensitive to POC both on and within the filter matrix (Chen et al., 2004; Chow et al., 2004).

EC by optical signals is reported separately in the database by R, T, and wavelength. For example, ECR1 is EC by reflectance of laser #1, the 635 nm reference laser, and ECT7 is EC by transmittance of laser #7, 980 nm. In general, ECR is higher than ECT due to organic vapors pyrolyzed within the filter evolving after native EC and POC on the surface (Chen et al., 2015b). There are two competing factors affecting the time when the R and T signals
return to baseline: the native BrC and the POC. The native BrC causes shorter wavelengths to have a lower baseline, causing the R and T to return to baseline earlier than longer wavelength. If the POC absorbs stronger at shorter wavelength, the POC may delay the shorter wavelength returning to baseline, causing the R and T to return to baseline later than longer wavelength.

Table 4-1 compares ECR and ECT at 635 nm with the six new wavelengths available to the Model 2015 for 137 Fresno samples. ECRs compare well with the exception of 532 nm, which originally suffered from poor signal to noise ratio. It has since been upgraded and new data are being acquired. Splits at shorter wavelengths show sensitivity to BrC, evidenced by larger ECR at 405 and 445 than at 635 nm. Therefore, it seems that the native BrC has more influence than the POC on shorter wavelength R for these samples. ECT for longer wavelengths have higher values than 635 nm, consistent with ECT being influenced more by POC within the filter matrix than native BrC on the filter surface. This causes decreasing ECT with decreasing wavelength.

Table 4-1: Fresno ambient samples analyzed by Model 2015 for optical pyrolysis. x and y are wavelengths of the seven-wavelength light source; x is 635 nm and y are the new wavelengths available for analysis. This table shows comparisons of new wavelengths to the 635 nm. m and b are Deming regression slope and intercept. n=137.

<table>
<thead>
<tr>
<th>Optical Split (nm)</th>
<th>Average (μg/cm²)</th>
<th>Corr.</th>
<th>Deming: y=mx+b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
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<tr>
<td>635 405</td>
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<td>0.93</td>
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<tr>
<td>445 5.01</td>
<td>0.98</td>
<td>1.06</td>
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<td>0.62</td>
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<td>-0.57</td>
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<td>0.90</td>
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<td>0.92</td>
<td>1.04</td>
<td>-0.01</td>
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<td>ECT</td>
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</tr>
<tr>
<td>635 405</td>
<td>2.90</td>
<td>0.91</td>
<td>1.30</td>
</tr>
<tr>
<td>445 2.97</td>
<td>0.99</td>
<td>1.07</td>
<td>-0.33</td>
</tr>
<tr>
<td>532 2.69</td>
<td>0.98</td>
<td>0.97</td>
<td>-0.14</td>
</tr>
<tr>
<td>780 3.18</td>
<td>1.00</td>
<td>1.03</td>
<td>0.19</td>
</tr>
<tr>
<td>808 3.25</td>
<td>1.00</td>
<td>1.06</td>
<td>0.19</td>
</tr>
<tr>
<td>980 3.47</td>
<td>0.99</td>
<td>1.09</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Tables 4-2 and 4-3 compare ECR and ECT at 635 nm to the six new wavelengths as well, divided by source type. The source samples analyzed for optical calibration in Section 3.2 are used here. Sources dominated by BC, i.e. diesel exhaust and flaming pine needles, showed relatively constant ECR and ECT across the wavelength range, consistent with the almost exclusive contribution of EC to light absorption. Smoldering biomass samples show increasing ECR with decreasing wavelength, indicating enhanced sensitivity to absorption by BrC at shorter wavelengths, especially the pine cone ECR.

Table 4-2: ECR for source samples.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Optical Split (nm)</th>
<th>Average (µg/cm²)</th>
<th>Corr. y=mx+b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>r²</td>
</tr>
<tr>
<td>Diesel</td>
<td>635</td>
<td>405</td>
<td>7.42</td>
</tr>
<tr>
<td>Exhaust</td>
<td></td>
<td></td>
<td>7.62</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td></td>
<td>7.01</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td></td>
<td>7.50</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td></td>
<td>7.48</td>
</tr>
<tr>
<td></td>
<td>808</td>
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<td>7.41</td>
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<tr>
<td></td>
<td>980</td>
<td></td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>635</td>
<td>405</td>
<td>10.95</td>
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<tr>
<td></td>
<td>445</td>
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<td>10.77</td>
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<td>6.34</td>
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<td>780</td>
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<td>808</td>
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<tr>
<td></td>
<td>980</td>
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<td>10.52</td>
</tr>
<tr>
<td>Smoldering Pine Cone</td>
<td>635</td>
<td>405</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td></td>
<td>7.35</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td></td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td></td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td></td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td></td>
<td>3.21</td>
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<tr>
<td>Smoldering Peat Cone</td>
<td>635</td>
<td>405</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td></td>
<td>4.44</td>
</tr>
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<td></td>
<td>532</td>
<td></td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td></td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>
Table 4-3: ECT for source samples.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Optical Split (nm)</th>
<th>Average (μg/cm²)</th>
<th>Corr.</th>
<th>Deming: y=mx+b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>r²</td>
<td>m</td>
</tr>
<tr>
<td>ECT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel Exhaust</td>
<td>635 405</td>
<td>7.01 7.38</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>7.17</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>6.97</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>6.96</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td>6.96</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>7.07</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>Flaming Pine Needle</td>
<td>635 405</td>
<td>9.10 8.93</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>8.87</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>8.82</td>
<td>1.00</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>9.40</td>
<td>0.99</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td>9.68</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>10.07</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>Smoldering Peat</td>
<td>635 405</td>
<td>2.83 2.54</td>
<td>0.75</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>2.00</td>
<td>0.81</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>2.93</td>
<td>1.00</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>4.46</td>
<td>0.89</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td>5.63</td>
<td>-0.25</td>
<td>10.92</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>7.32</td>
<td>0.30</td>
<td>1.74</td>
</tr>
<tr>
<td>Smoldering Pine Cone</td>
<td>635 405</td>
<td>0.79 3.62</td>
<td>-0.59</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>1.87</td>
<td>-0.54</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.17</td>
<td>-0.36</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>0.78</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>808</td>
<td>0.78</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>0.78</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

ECT is expected to decrease with wavelength since the multiple-scattering effect is larger for shorter wavelengths. On the other hand, Chow et al (1993) observed that the operational definition for EC by any TOA protocol might contain some light-absorbing OC. BrC, if present, would lower the pre-analysis values of R and T for shorter wavelengths, resulting in earlier split points and larger EC reported than that from longer wavelengths. ECT data show that longer wavelengths indeed show higher ECT values for smoldering peat. Data from smoldering pine cone show that nearly all EC came from POC and so the ECT analysis here is inconclusive. Further study of smoldering biomass is suggested.
4.2 Absorption Efficiencies and Apportionment of EC and POC in Ambient Samples

Thermal/optical carbon analyzers traditionally make use of a single wavelength laser to monitor the filter sample for charring. The Model 2015 with its seven-wavelength light source allows monitoring optical properties of the filter across a broad spectrum, and value is added to analysis results by incorporating this new information.

This study investigates how POC behaves optically at these wavelengths. Chow et al. (2004) investigated absorption efficiencies of EC and POC at 632.8 nm and found that it is possible to partition EC and POC by estimating light absorption by an aerosol deposit compared to that of the blank filter. Adapting the techniques described in Chow et al. (2004), each Model 2015 wavelength was studied separately to estimate absorption efficiencies of EC and POC. Partitions based on these efficiencies were compared to EC measured by TOR/TOT charring corrections.

4.2.1 Methods

More than three hundred samples from the Fresno supersite were analyzed by the Model 2015. For this study, samples were selected whose laser signals at all wavelengths were recoverable throughout the analysis: no errors were recorded in the database for pyrolysis, drift was minimal and signals were still detectable at maximum charring (i.e., lowest possible transmittance values must be above the detection limit). Approximately 140 Fresno samples met these criteria.

To calculate absorption efficiencies, attenuation due to EC and POC ($\tau_{ATN,EC}$ and $\tau_{ATN,POC}$, respectively) were calculated by

$$\tau_{ATN,EC} = -\ln \frac{T_i}{T_f} \quad (4-1)$$

$$\tau_{ATN,POC} = -\ln \frac{T(t)}{T_i} \quad (4-2)$$

where $T_i$ is the initial transmittance intensity before heating of the filter, $T_f$ is the transmittance intensity at the end of analysis, i.e., the transmittance of the blank filter, and $T(t)$ is the transmittance value at any instant before EC and POC evolve, detected by an
increase in transmittance signal. For this study, \( T(t) \) is taken to be the minimum positive nonzero transmittance value in the OC4 fraction. Carbon evolved after \( O_2 \) is assumed to be the sum of POC and EC. The equations for absorption efficiencies (EA) become

\[
E_{A,EC} \left( \frac{g}{m^2} \right) = \frac{\tau_{ATN,EC}}{[EC]} \tag{4-3}
\]

\[
E_{A,POC} \left( \frac{g}{m^2} \right) = \frac{\tau_{ATN,POC}}{[POC]} \tag{4-4}
\]

and

\[
[carbon]_{after \ O_2} = [EC] + [POC] = \frac{\tau_{ATN,EC}}{E_{A,EC}} + \frac{\tau_{ATN,POC}}{E_{A,POC}} \tag{4-5}
\]

Here \([EC]\), \([POC]\), \(E_{A,EC}\) and \(E_{A,POC}\) are unknowns, and they are calculated by regression analysis of \([carbon]_{after \ O_2}\) on \(\tau_{ATN,EC}\) and \(\tau_{ATN,POC}\). Intercept is set to zero and the inverse of the regression coefficients are the estimated absorption efficiencies, i.e., \(E_{A,POC}\) and \(E_{A,EC}\).

The ratio of absorption efficiencies \(E_{A,POC}/E_{A,EC}\) is representative of the POC and EC absorption property similarity (Moosmüller et al., 2009; Moosmüller and Chakrabarty, 2011). A ratio close to unity indicates that POC is behaving optically more like EC at that wavelength, meeting the second assumption for char correction stated previously, and therefore would be good candidates for improving char correction.

Microsoft Excel’s built-in data analysis package was used to perform multiple linear regression on the data. The applet takes total carbon after \( O_2 \) injection as its y-input, \(\tau_{EC}\) as its x1-input, and \(\tau_{POC}\) as its x2-input. \(R^2\) for all analyses was 0.97 or higher.

The \(E_{A,POC}/E_{A,EC}\) ratios from regression at each wavelength are then used to partition EC and POC on a per-sample basis with Equation 4-5. Thirty random samples were chosen for the partition graphs. These charts are overlaid with the OC/EC splits determined from reflectance and transmittance.

4.2.2 Results and Discussion

Figure 4-1a through 4-1g show the comparison of \([carbon]\) after \( O_2 \) injection with the maximum attenuation observed during the analysis. Table 4-4 lists \(E_{A,POC}, E_{A,EC}\), and their ratios obtained from multilinear regression of the Fresno samples. Note that the
E_{A,POC}/E_{A,EC} ratio generally decreases with increasing wavelength. The E_{A,POC} at shorter wavelengths (e.g., 405 nm) are significantly higher than E_{A,EC}, which may be due to the presence of light-absorbing OC on the filter prior to thermal analysis. Even in the absence of light-absorbing OC, E_{A,POC}/E_{A,EC} ratios may be higher at shorter wavelengths due to increased multiple scattering effects within the filter (Chen et al., 2015). Data points in Figure 4-1a through 4-1g are bounded by the estimates of E_{A,POC} and E_{A,EC}. These lines closely bracket the upper and lower edges of the data points for wavelengths above 532 nm, but the regression E_{A,POC} lines are higher than the data points for 405 and 445 nm. This may indicate a limitation of the model for wavelengths sensitive to light-absorbing OC present on the filter before thermal analysis. Equation 4-5 is valid at longer wavelengths where BrC does not absorb strongly. BrC absorption can be taken into account by considering an additional equation for the model:

\[
[\text{carbon}]_{initial} = [EC] + [BrC] = \frac{\tau_{ATN,EC}}{E_{A,EC}} + \frac{\tau_{ATN,BrC}}{E_{A,BrC}}
\]  

(4-6)

The standard wavelength 635 nm in the IMPROVE_A protocol has a E_{A,POC}/E_{A,EC} ratio of 3.2, somewhat higher than longer wavelengths (e.g., E_{A,POC}/E_{A,EC} = 2.2 for 980 nm). Therefore, with the current Model 2015 wavelengths, char correction at 980 nm may be preferable while still reporting 635 for equivalence to be consistent with the long-term networks.

Table 4-4: Absorption efficiencies of EC and POC and their ratios per wavelength for the Fresno samples.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>E_{A,EC}</th>
<th>E_{A,POC}</th>
<th>E_{A,POC}/E_{A,EC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>405</td>
<td>33.8 ± 1.1</td>
<td>470.9 ± 130.8</td>
<td>13.9</td>
</tr>
<tr>
<td>445</td>
<td>31.2 ± 1.2</td>
<td>162.3 ± 24.3</td>
<td>5.0</td>
</tr>
<tr>
<td>532</td>
<td>30.4 ± 1.8</td>
<td>78.1 ± 8.4</td>
<td>2.6</td>
</tr>
<tr>
<td>635</td>
<td>25.07 ± 1.2</td>
<td>81.04 ± 9.2</td>
<td>3.2</td>
</tr>
<tr>
<td>780</td>
<td>22.2 ± 1.2</td>
<td>54.6 ± 5.5</td>
<td>2.5</td>
</tr>
<tr>
<td>808</td>
<td>21.3 ± 1.0</td>
<td>55.5 ± 5.8</td>
<td>2.6</td>
</tr>
<tr>
<td>980</td>
<td>18.7 ± 1.0</td>
<td>40.6 ± 4.0</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 4-2a through 4-2g show the partitioning of EC and POC determined by ratios of absorption efficiencies in Table 4-4, calculated individually as
\[ [EC] = \frac{\tau_{ATN, EC}}{E_{A,EC}} \]  
\[ [POC] = \frac{\tau_{ATN, POC}}{E_{A,POC}} \]

and overlaid with the amount of EC determined by reflectance (ECR) and transmittance (ECT) for each wavelength. Table 4-5 lists the regression between ECR and ECT with partitioned EC. Similar to the findings by Chow et al. (2004), ECR agrees with partitioned EC for most samples at 635 nm, while ECT is lower than ECR. Shorter wavelengths are biased towards lower POC when partitioned in this manner, and both ECR and ECT are lower than partitioned EC. The model needs to be refined by incorporating both Equations 4-5 and 4-6 to account for BrC, POC, and EC.

Finally, absorption Angstrom exponents (AAE) were calculated by power law regression through the absorption efficiencies plotted against wavelength as shown in Figure 4-3. Efficiencies were normalized to 635 nm which has no effect on the exponent or the \( r^2 \) of the regression. AAE for EC was 0.7 \( (r^2=0.99) \) while AAE for POC was 2.3 \( (r^2=0.81) \). AAE greater than 1 for POC shows that it does not behave as EC and may retain some light absorbing organic compounds through the pyrolysis stage.
Figure 4-1a: Comparison of [carbon] after O$_2$ with the maximum attenuation at 635 nm. The absorption efficiencies of EC and POC are estimated from multiple linear regression.

Figure 4-1b: Comparison of [carbon] after O$_2$ with the maximum attenuation at 405 nm.
Figure 4-1c: Comparison of [carbon] after O\textsubscript{2} with the maximum attenuation at 445 nm.

Figure 4-1d: Comparison of [carbon] after O\textsubscript{2} with the maximum attenuation at 532 nm.
Figure 4-1e: Comparison of [carbon] after O₂ with the maximum attenuation at 780 nm.

Figure 4-1f: Comparison of [carbon] after O₂ with the maximum attenuation at 808 nm.
Figure 4-1g: Comparison of [carbon] after O$_2$ with the maximum attenuation at 980 nm.

Figure 4-2a: EC/POC partition at 405 nm. Red and black overlays are EC from transmittance and reflectance, respectively.
Figure 4-2b: EC/POC partition at 445 nm.

Figure 4-2c: EC/POC partition at 445 nm.
Figure 4-2d: EC/POC partition at 532 nm.

Figure 4-2e: EC/POC partition at 780 nm.
Figure 4-2f: EC/POC partition at 808 nm.

Figure 4-2g: EC/POC partition at 980 nm.
Table 4-5: Regression of ECR and ECT vs. partitioned EC at each wavelength.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>ECR ($\mu$g/cm$^2$)</th>
<th>ECT ($\mu$g/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m (\pm \sigma)$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>405</td>
<td>0.86±0.02</td>
<td>0.95</td>
</tr>
<tr>
<td>445</td>
<td>0.92±0.02</td>
<td>0.96</td>
</tr>
<tr>
<td>532</td>
<td>0.86±0.03</td>
<td>0.89</td>
</tr>
<tr>
<td><strong>635</strong></td>
<td><strong>1.02±0.02</strong></td>
<td><strong>0.96</strong></td>
</tr>
<tr>
<td>780</td>
<td>1.06±0.02</td>
<td>0.96</td>
</tr>
<tr>
<td>808</td>
<td>1.08±0.02</td>
<td>0.95</td>
</tr>
<tr>
<td>980</td>
<td>1.09±0.03</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 4-3: Power law regression for determining AAE of EC and POC based on absorption efficiencies (n=139).

### 4.3 Preliminary Testing with Different Thermal/Optical Protocols

4.3.1 Description and implementation of different protocols

OC and EC are operationally defined by the instrument and protocol used for analysis. Previous studies have shown that while TC are comparable among protocols, OC and EC can be quite different (Schmid et al., 2001; Watson et al., 2005). As shown in Table 4-6, protocols are different in: 1) temperature plateaus, 2) residence time at each plateau, and
3) optical monitoring configurations and wavelength. Several earlier comparison studies of different protocols were performed on different instruments. The observed differences have confounding influences from different protocols as well as from different instruments (Schmid et al., 2001; Watson et al., 2005). Therefore, it will be ideal to compare all protocols on one single instrument to remove the inter-instrument differences.

The Model 2015 is designed to run user-specified thermal/optical protocols, including several already described in the literature. This is accomplished by a protocol customization module in the software along with temperature ramping parameters optimized for each protocol. Research Objective #4 of this study is to demonstrate the Model 2015’s performance while running IMPROVE_A, NIOSH, STN, and EUSAAR_2 protocols. Approximately fifteen archived Fresno samples were analyzed on each of the four protocols on a single instrument. A brief discussion on the OC/EC split and comparisons of total carbon follows, though a systematic study of more samples, including ambient rural, urban, and source samples is still needed to compare the differences between protocols, and potentially optimize a protocol that can be more accurate than all existing protocols. This future work is restated in Section 5.1.

Table 4-6: Comparison of thermal/optical protocols (adapted from Chow et. al., 2001 and 2014).

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>IMPROVE_A TOR</th>
<th>NIOSH TOT</th>
<th>STN TOT</th>
<th>EUSAAR_2 TOT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>Residence Time (t_r, sec)</td>
<td>Temp</td>
<td>t_r</td>
</tr>
<tr>
<td>OC1 Inert (He)</td>
<td>140</td>
<td>80-580</td>
<td>250</td>
<td>150</td>
</tr>
<tr>
<td>OC2 Inert</td>
<td>280</td>
<td>80-580</td>
<td>500</td>
<td>150</td>
</tr>
<tr>
<td>OC3 Inert</td>
<td>480</td>
<td>80-580</td>
<td>650</td>
<td>150</td>
</tr>
<tr>
<td>OC4 Inert</td>
<td>580</td>
<td>80-580</td>
<td>850</td>
<td>160</td>
</tr>
<tr>
<td>cool Inert</td>
<td>n/a</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>EC1 Oxidizing (2% O_2 in He)</td>
<td>580</td>
<td>80-580</td>
<td>650</td>
<td>150</td>
</tr>
<tr>
<td>EC2 Oxidizing</td>
<td>740</td>
<td>80-580</td>
<td>750</td>
<td>150</td>
</tr>
<tr>
<td>EC3 Oxidizing</td>
<td>840</td>
<td>80-580</td>
<td>850</td>
<td>150</td>
</tr>
<tr>
<td>EC4 Oxidizing</td>
<td>825</td>
<td>45</td>
<td>920</td>
<td>120</td>
</tr>
</tbody>
</table>

The temperature set points in carbon analysis protocols are motivated by accurately separating OC and EC while generating thermal fractions that contain information about particle source and chemical properties. Temperature- and analysis atmosphere-separated
carbon fractions are useful for aerosol source apportionment (Chow et al., 2005; Kim et al., 2004; Kim and Hopke, 2004). The temperatures specified by different protocols were established by examining the analysis needs. EUSAAR_2 specifies lower set points with longer residence times than NIOSH and STN in an effort to preferentially evolve OC rather than char it to POC. NIOSH uses the 850°C OC4 fraction to detect calcium carbonate from mining operations (Turpin et al., 1990), though Chow et al. (2001) showed that calcium carbonate can decompose at a temperature as low as 550 °C depending on the mineral form and associated impurities. Furthermore, such a high temperature plateau can prematurely evolve EC due to interference from oxidizing and/or catalyzing substances present on the filter.

Since protocols vary greatly in their temperature plateaus and residence times, OC/EC splits are seldom in agreement across different protocols. It is thought that the highest temperature step in the OC stage is a critical factor in the accuracy of the split (Conny et al., 2003). Each of the protocols used for this study has a different temperature plateau for the final OC stage: 580°C, 900°C, 650°C, and 850°C for IMPROVE_A (Figure 4-4a), NIOSH (b) STN (c), and EUSAAR_2 (d), respectively. Previous research summarized the reported effects of altering the peak OC temperature (Cavalli et al., 2010; Subramanian et al., 2006), and suggested that lower OC temperatures can increase measured EC due to OC neither completely evolving nor charring, while high OC temperatures can bias the OC/EC split due to premature EC evolution, perhaps due to the presence of mineral oxides. However, it is not conclusive what the highest OC4 temperature plateau should be. Subramanian et al. (2006) sought to minimize the effects of charring by extracting some OC prior to thermal analysis, similar to the approach described by Fung (1990). However, such sample pretreatment adds experimental complexity and introduces extra uncertainties.

Figure 4-4 shows that the Model 2015 successfully executed the IMPROVE_A, NIOSH, and EUSAAR_2 protocols. The STN protocol, however, is designed to rapidly reach high temperatures and stay for short residence times. The OC4 peak is 900°C for 90 seconds, and EC1, EC2, EC3, and EC4 are 600, 675, 750, 825°C, respectively, for 45 seconds each, and EC5 at 920°C for 120 seconds. It seems that these ramping times are not long enough
for the sample oven to plateau at the target temperatures. Thermograms generated by Model 2015 do not closely agree with those from Peterson and Richards (2002). A power supply with a higher output voltage may provide the heating power necessary to reach these high temperatures fast enough for the temperature to plateau and the fraction to evolve. Furthermore, with such rapid temperature changes, the transmittance detector must be tuned to ensure the lasers do not saturate.
Figure 4-4: Example thermograms for: a) IMPROVE_A, b) NIOSH, c) STN, and d) EUSAAR_2 thermal/optical protocols on Model 2015 for Fresno sample FSH00099.
4.3.2 Results

Figure 4-5 is the TC comparison of NIOSH, STN, and EUSAAR_2 to IMPROVE_A. TC agreed across all protocols, with slopes within one or two standard errors of unity. NIOSH TC closely agrees with IMPROVE_A, while STN and EUSAAR_2 TC were 7-10% higher.
Each protocol reports the OC/EC split based on either reflectance or transmittance. IMPROVE_A reports TOR while NIOSH, STN, and EUSAAR_2 report TOT. Figure 4-6 compares IMPROVE_A TOR to the other protocols’ TOT. Deming regression slope and intercept are shown along with their equations, and the 1:1 line is plotted for comparison. Deming regression slope and intercept of IMPROVE_A TOR vs. protocol TOT averaged across all seven wavelengths is shown in Table 4-7. When compared to IMPROVE_A TOR, OC is consistently overestimated by the three protocols while EC is underestimated. In particular, NIOSH reports slightly less than half the EC of IMPROVE_A, consistent with results from Chow et al. (2001). These large differences in OC and EC can be attributed to the influence of POC in the filter matrix to the transmittance signal.

Figure 4-5: TC comparison of the protocols.
Figure 4-6: Comparison of OCR/ ECR by IMPROVE_A with OCT/ECT by other protocols.

Table 4-7. OC and EC Deming statistics averaged across all seven wavelengths.

<table>
<thead>
<tr>
<th></th>
<th>NIOSH</th>
<th></th>
<th>STN</th>
<th></th>
<th>EUSAAR_2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>b</td>
<td>m</td>
<td>b</td>
<td>m</td>
<td>b</td>
</tr>
<tr>
<td>OC</td>
<td>1.13±0.07</td>
<td>2.33±1.19</td>
<td>1.21±0.15</td>
<td>0.83±20.9</td>
<td>1.19±0.17</td>
<td>-0.43±1.63</td>
</tr>
<tr>
<td>EC</td>
<td>0.47±0.13</td>
<td>-1.14±0.54</td>
<td>0.55±0.18</td>
<td>-0.13±0.79</td>
<td>0.68±0.13</td>
<td>-0.06±0.38</td>
</tr>
</tbody>
</table>

TOR (Figure 4-7a-n, Table 4-8) and TOT (Figure 4-8a-n, Table 4-9) across all protocols were also compared. Slopes compared favorably across all protocols with values usually within one standard deviation of unity, though again NIOSH and STN were biased towards high OC.

As shown in the ECR and ECT graphs in Figures 4-7 and 4-8, in the case of lightly-loaded filters the high-temperature protocols often measured a negative value of EC. In these cases, most if not all native EC was pyrolyzed and evolved from the filter before the sample was exposed to the oxidizing environment.
Figure 4-7: Comparison of TOR by all protocols and wavelengths.

Table 4-8: Summary of TOR statistics averaged across all wavelengths.

<table>
<thead>
<tr>
<th>TOR</th>
<th>NIOSH</th>
<th>STN</th>
<th>EUSAAR_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m</td>
<td>b</td>
<td>m</td>
</tr>
<tr>
<td>OC</td>
<td>1.03±0.14</td>
<td>5.26±2.03</td>
<td>0.95±0.10</td>
</tr>
<tr>
<td>EC</td>
<td>1.15±0.33</td>
<td>-4.98±1.53</td>
<td>1.54±0.33</td>
</tr>
</tbody>
</table>
Figure 4-8: Comparison of TOT by all protocols and wavelengths.

Table 4-9: Summary of TOT statistics averaged across all wavelengths.

<table>
<thead>
<tr>
<th>TOT</th>
<th>NIOSH</th>
<th>STN</th>
<th>EUSAAR_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>b</td>
<td>m</td>
</tr>
<tr>
<td>OC</td>
<td>1.00±0.06</td>
<td>2.96±1.04</td>
<td>1.07±0.10</td>
</tr>
<tr>
<td>EC</td>
<td>1.22±0.44</td>
<td>-1.85±1.09</td>
<td>1.68±0.85</td>
</tr>
</tbody>
</table>
Many additional samples are needed to be statistically significant in these protocol comparisons. An additional 15-50 samples will provide a dataset large enough to identify trends and potentially determine a unified protocol that performs better than the four studied. An investigation of the OC/EC split of samples that are preferentially loaded with BrC or BC such as source samples would add value to the multiwavelength data. This is discussed further in Section 5.1.

4.4 Summary

Replicate analysis performed on archived network samples by the Model 2015 yielded a large data set with a wealth of multiwavelength optical data. Adapting techniques from Chow et al. (2004), absorption efficiencies of EC and POC at each wavelength were individually investigated. The $E_{A,POC}/E_{A,EC}$ ratio is used as a proxy for the ratio of scattering cross sections. A ratio of 3.2 was observed for 635 nm, the standard wavelength used for char correction. A ratio of 13.9 was observed for 405 nm, indicating that additional considerations be taken when investigating wavelengths sensitive to light-absorbing OC. A ratio of 2.2 was observed for 980 nm, indicating that longer wavelengths may be better candidates for performing char correction than 635 nm, while still reporting 635 nm for equivalence with legacy instruments.

Preliminary testing was done to compare different thermal protocols (IMPROVE_A, NIOSH, STN, EUSAAR_2) on the Model 2015. Of interest are the effects of the highest temperature plateau in the OC stage and its effects on the OC/EC split. It was found that TC compared well (±10%) among the different protocols while OC and EC varied greatly. Even protocols with similar temperature plateaus such as STN and NIOSH showed large differences in pyrolysis fractions and their OC/EC split. It was determined that the instrument design need be taken into consideration when performing high-temperature protocols such as STN and NIOSH, as the heating element may not be able to reach the temperature steps within the time allotted by the protocol. Additional samples have been identified for analysis with the four protocols.
5 CONCLUSIONS AND FUTURE WORK

A modern instrument, the DRI Model 2015 Multiwavelength Carbon Analyzer, has been designed and developed to analyze OC and EC and their thermal fractions. Two units, designated CA17 and CA21, were built, calibrated, characterized, and put in to service as laboratory instruments for research analysis to investigate the utility of multiwavelength data combined with thermal analysis. The multiwavelength feature allows this instrument to further investigate the wavelength-dependent nature of BrC and BC on quartz-fiber filter samples. The design process emphasized ease of construction, maintenance, and operation, with a minimum of proprietary components and fewer reagents needed compared to previous instruments. CA17 and CA21 were used extensively to characterize the behavior of the instrument and to analyze ambient and source samples to both demonstrate equivalence to legacy instruments and to investigate the value of multiwavelength data. Optical properties of source samples were investigated and comparisons of different thermal protocols were performed.

Absorption efficiencies of EC and POC as a function of wavelength were calculated from incremental attenuation of the filter throughout analysis, and ratios of scattering cross sections ($\sigma_{EC}$ and $\sigma_{POC}$) were inferred. From these ratios it was determined that 980 nm may be a better candidate to monitor char correction, as EC and POC exhibit similar optical behavior with increasing wavelength. $E_{A,POC}/E_{A,EC}$ ratios at shorter wavelengths suggest that additional physics for wavelengths sensitive to light absorbing OC be considered, and the potential partitioning of a filter sample into BC, BrC, and POC as a function of analysis time is suggested as a future development of this work.

A small set of samples were selected for analysis by different thermal protocols (IMPROVE_A, NIOSH, STN, and EUSAAR_2) to compare OC/EC splits and pyrolysis fractions as a function of wavelength and temperature. While TC compared well among the protocols, OC, EC, LTPY($\lambda$) and LRPY($\lambda$) did not, and additional samples have been identified in order to form a statistically-significant data set to compare trends in these disparate fractions.
As a laboratory instrument, the Model 2015 needs to be put into continuous, long-term use. The Model 2001 has been in nearly continuous use for more than a decade, in many instances operating around the clock for weeks or months at a time. Currently, there are plans to build enough analyzers to re-fit the carbon analysis laboratory at EAF with Model 2015. A long period of heavy use will further characterize the instrument.

Future scientific work includes proliferation of the Model 2015 to laboratories around the world in order to bring multi-wavelength analysis capabilities to other research groups and agencies. Replicate analysis of old samples may lead to better understanding of the contributions of brown and black carbon to previous air quality trends and events.

### 5.1 Future research questions

This section outlines possible future work to be done in characterizing the Model 2015 and determining the value of the multiwavelength data. In some cases, initial work has been done and it is detailed here.

#### 5.1.1 Black carbon aggregates on filter media during thermal evolution

Freshly-emitted black carbon can be thought of as “fluffy” long-chain fractal aggregates that collapse into spherical soot clusters as they age in the atmosphere. Such clusters gathered on quartz-fiber filters during routine sampling may be comprised of geometries spanning these two extremes with varying intensive properties. During thermal analysis, it is possible that soot clusters are being liberated into long-chain aggregates. This could manifest as slight changes in optical properties throughout the analysis. Multiwavelength data could be used to explore this phenomenon.

#### 5.1.2 Additional considerations for the multiwavelength light source

This study focused on the seven wavelengths in the Model 2015 from 405 to 980 nm. These were chosen due to their cost, package, availability, output power, voltage requirements, stability, and longevity and to span a sufficient wavelength range. However, as laser technology moves forward, more wavelengths may become available that meet said requirements. This would bring an opportunity to investigate aerosol optical physics beyond the capabilities of the current system.
5.1.3 Partitioning BC, BrC, and POC
In Section 4.2.2, ratios of absorption efficiencies were investigated and it was found that short wavelengths such as 405 and 445 nm had high ratios not commensurate with the comparison of carbon evolved after oxygenation of the analysis environment and maximum attenuation during charring. Since these wavelengths are sensitive to light-absorbing OC, this suggests that the model used by Chow et al (2004) be modified to include a term for BrC. In particular, Equations 4-5 and 4-6 could be used together to fully partition a sample into BC, BrC, and POC.

5.1.4 Use of multiwavelength reflectance data
The majority of this study focused on transmittance data. However, while reflectance measured by Model 2015 depends on scattering, it is more representative of the albedo of the filter surface than scattering by particles (Chen, personal communication). Filter albedo is related to particle scattering and absorption. A more appropriate framework is a two-stream radiative transfer model (Bohren, 1987) and Kubelka-Munk theory (Kubelka and Munk, 1931) to determine scattering (and absorption) efficiency (Chen et al., 2004; Chen et al., 2015a) based on reflectance and transmittance measurements. Such an analysis would be beneficial to determining how multi-wavelength data can be used to refine measurements of optical properties.

5.1.5 Functionality of the side-arm oxygen injector
The updated Model 2015 quartz cross oven has a larger cavity for MnO₂ as well as an additional inlet (“side-arm’) for the He2 or He/O₂ flow. This side-arm ensures that there is O₂ passing through the oxidation oven to ensure complete oxidation of OC to CO₂: during the OC stage, O₂ is sent through the side arm to the oxidation oven; during the EC stages, O₂ is sent through the sample oven, and the residual O₂ will pass through the oxidation oven. MnO₂ is an efficient oxidation agent. However, it degrades over time after being consumed and changing to lower oxidation states such as Mn₃O₄ (tri-manganese tetroxide) and Mn₂O₃ (Manganese sesquioxide) (Fung et al., 2002). This degradation will cause different oxidation efficiencies in the OC and EC stage with the single-bulb oven design of the Model 2001, thereby causing bias in OC and EC quantification. With the presence
of \(O_2\) in the oxidation oven, \(O_2\) also serve as the oxidation agent. Therefore, high oxidation efficiency is maintained for both OC and EC stages, and the MnO\(_2\) lifespan is increased. However, this design raises two questions:

1) What are the oxidation efficiencies and MnO\(_2\) life span with and without the side arm \(O_2\) injection?

2) Is it possible that \(O_2\) may be diffusing upstream toward the filter sample and altering the analysis environment, oxidizing the sample too early?

To address the first question, MnO\(_2\) with various usage times is needed to represent different degradation status. Fresh MnO\(_2\) oxidizes all carbon to CO\(_2\) without the aid of extra \(O_2\). To test the efficiency of aged MnO\(_2\) with the \(O_2\) supplement, a long-term study must be conducted. The Model 2015 is new enough that there currently are no reactors old enough for this study.

To characterize any possible interference from \(O_2\) diffusion towards the sample from the side-arm, a 10 \(\mu\)l sucrose standard solution was spiked on a blank filter and was analyzed with a modified IMPROVE_A protocol that forces the OC4 stage to run for 1200 seconds. OC4 is a high temperature inert environment stage and should ideally not release any char or EC, and the R and T signals should not increase. An increase in R and T signals along with release of carbon indicates that \(O_2\) might be present at the sample oxidizing POC and EC. To compare, the same test was run on a Model 2015 analyzer modified so that only helium was injected into the side-arm. Each test was run two or three times to ensure confidence.

In all cases (two with \(O_2\), three without) the NDIR signal fell to less than 1ppm over the course of the extended OC4 fraction. No significant changes in the NDIR final and initial readings were detected in the tests. OC4 fraction percentage of TC was similar across all tests.
Table 5-1: Summary of NDIR results for the five tests (average ± standard deviation).

<table>
<thead>
<tr>
<th>State</th>
<th>% carbon in OC4</th>
<th>NDIRI</th>
<th>NDIRF</th>
<th>NDIR Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ available</td>
<td>9.71 ± 0.14</td>
<td>1.46 ± 0.09</td>
<td>0.20 ± 0.09</td>
<td>-1.26 ± 0.001</td>
</tr>
<tr>
<td>No O₂</td>
<td>10.53 ± 0.71</td>
<td>1.5 ± 0.08</td>
<td>0.34 ± 0.04</td>
<td>-1.17 ± 0.07</td>
</tr>
</tbody>
</table>

Chromatograms from routine O₂ testing show that with O₂ available to the oxygenator reactor, the concentration of O₂ upstream near the sample is approximately 1 ppm, which is within acceptable limits per the Standard Operating Procedure (DRI, 2015). A chromatogram was then taken from a completely inert environment with the side-arm switched off. Oxygen concentration was still below 1 ppm.

Figure 5-1: Chromatogram with oxygen available through the side-arm.
Figure 5-2: Chromatogram with side-arm switched off
6 REFERENCES


7 APPENDICES

7.1 Appendix I – Electrical Schematic and Layout of the Laser PCB

This section details Version 6 of the laser PCB. It was designed in KiCad (an open-source Eagle variant designed and maintained by the European Organization for Nuclear Research) and manufactured by Bittele Electronics, Incorporated (Toronto, Canada).

KiCad utilizes a hierarchical design paradigm. The first sheet of a KiCad schematic is the hierarchy, showing how subsequent sheets interconnect. Figures 7.1a through e show the schematic and Figure 7.1f shows the layout of the board.

![Figure 7-1a: The hierarchy of the laser PCB.](image-url)
Figure 7-1b: The microcontroller sheet. This sheet has connections pertaining to the Atmel ATMEGA328P microcontroller which modulates the lasers and outputs reference and timing signals. Associated circuitry includes its power supply, pull-down resistors for the load switches, the ICSP header, and two switches for manually activating the lasers and resetting the microcontroller.
Figure 7-1c: the load switches, indicator LEDs, and connector block.
Figure 7-1d: The subtracting amplifier and its power supply.

Figure 7-1e: The connectors for all sensors, power input, and NI-DAQ interface.
Figure 7-1f: The physical layout of the laser PCB. Top copper layer is in red, through-hole components are in yellow, and bottom copper layer is in green. Annotations are internal to KiCad and do not print on the silkscreen layer.
7.2 Appendix II – Multiwavelength Retrofit for Model 2001 Analyzers

A multiwavelength upgrade to existing Model 2001 analyzers was developed before the Model 2015 was completed. Two versions of the retrofit were made. The first (Figure 7-2) contains a laser modulation PCB functionally identical to the ones found in Model 2015 and a USB NI-DAQ (National Instruments USB-6216) that interfaces to a separate LabView program that passes data to the standard DRICarb software. It is fully enclosed with ports to access power, computer connections, and potentiometers for R/T amplification.

The second version (Figure 7-3) is a drop-in replacement for the Model 2001’s entire optical system and has a laser control board that includes a pass-through very high density cable interconnect (VHDCI) connector that allows the Model 2001 to connect directly to the retrofit. Then all signals are passed to a National Instruments DAQ (PCIe-6341, identical to Model 2015). The arrangement of components is compact enough that it can fit comfortably in the Model 2015 once the He-Ne laser is removed (Figure 7-4). Several arrangements of components on the platform were investigated, hence the differences between Figure 7-2 and Figure 7-3.
Figure 7-2: Photograph of the first retrofit unit. This unit was installed at a laboratory in Rostock, Germany.

Figure 7-3: The drop-in replacement retrofit with VHDCI pass-through from Model 2001 to LabView.
Figure 7-4: The drop-in retrofit installed in Model 2001 with components labeled.